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KEYS TO ORGANIC CHEMISTRY

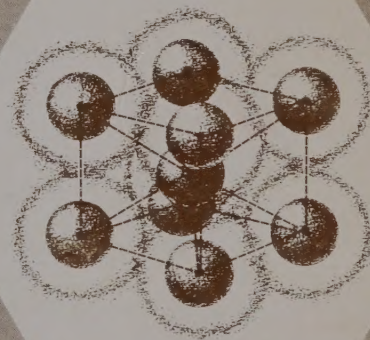
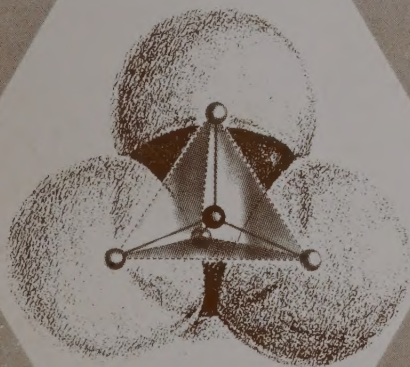
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A Module in the KEYS TO CHEMISTRY Program



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RATIONALE FOR THE KEYS TO CHEMISTRY

The core of the KEYS TO CHEMISTRY program is contained in the textbook and laboratory manual. However, supplementary modules have been developed to do the following things: (1) to expose interested and capable students to more sophisticated concepts in chemistry not included in the core program; (2) to expose students to some of the interesting applications of chemistry in daily living, including those aspects that might lead to chemistry-related careers and avocations. By selecting modules that fit their own goals and interests, students can plan a truly individualized chemistry course.

In many ways, the KEYS TO CHEMISTRY MODULES are patterned after the chapters in the core text. For example, each module provides students with a *Suggested Order of Study*, *Objectives*, *Suggestions for Further Study*, and an annotated *Bibliography*. In addition, the KEYS TO OXIDATION-REDUCTION module contains *Practice Exercises* and a *Self Test*. In each of the modules, questions are included with laboratory activities. Teachers can use students' laboratory data, along with their answers to laboratory questions, as an instrument for evaluating student learning.

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KEYS TO ORGANIC CHEMISTRY

LEON B. GORTLER • ROBERT C. TRIPP

JAY A. YOUNG • ELAINE W. LEDBETTER

PHILLIP H. CAMPBELL
Calgary, Alberta
Consultant, Revised Edition

A Module in the KEYS TO CHEMISTRY Program

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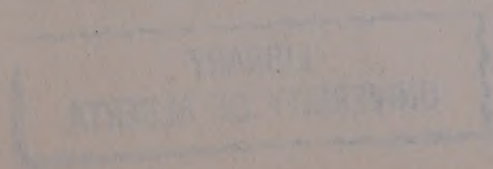


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INTRODUCTION

Chances are that you haven't thought much about the subject of organic chemistry. Few of us, for example, think about the fact that hundreds of reactions involving organic molecules occur within our bodies every minute. In fact, you can't make a move without organic chemicals—your muscles are made of proteins, which are organic molecules; the energy for muscle contraction is supplied by sugars, which are also organic molecules; and the oxygen required by muscle cells is transported through the blood by hemoglobin, another organic molecule.

The gasoline we use in our cars is organic. We heat our houses with wood, coal, oil, or natural gas—all organic fuels. We wash our clothing with soaps and detergents—organic compounds. In fact, the clothes are made of organic fibers like wool, cotton, linen, nylon, Orlon, and Acrilan.

Our health-oriented society consumes vast quantities of vitamins. Our medicines include aspirin, penicillin, tranquilizers. We use ethyl alcohol as an antiseptic, a solvent, a beverage. We use spices (cinnamon, cloves), flavorings (oil of wintergreen, vanilla), and preservatives (BHT, calcium propionate) in our foods. Our farmers use pesticides to help insure high crop production. All of these substances are organic compounds.

It's hard to imagine our lives without plastics and other synthetic polymers. These substances are made by bonding together simple organic molecules into long chains. Plastics, in the form of flexible or rigid sheets, are used in packaging, furniture, automobiles, toys, tools, paints, glues, and you-name-it.

We use suntan lotions, weed killers, plastic bags—they're all organic. Everything from moth balls to macaroni is organic.

The purpose of this module is to help you recognize and classify organic molecules, discover the relationships between their structures and properties, and see how they influence your daily life. It would be most interesting to start our study with foods, drugs and plastics. But these compounds are often complex. So we'll start with some of the simpler organic molecules and work our way up.

SUGGESTED ORDER OF STUDY

A glance through the Table of Contents of this module will give you an overview of the module's scope and sequence. Parts One through Three cover topics fundamental to the study of organic chemistry. These topics include the nature of the carbon atom and its bonding properties, a study of some classes of organic compounds, and an overview of the major organic functional groups. Parts One through Three are basic to the study of organic chemistry—they should be completed before Parts Four through Six.

Your order of study of this module will depend on the amount of time available. If you have time to complete the entire module, do so by progressing sequentially from Part One through Part Six. If you cannot complete the entire module, complete Parts One through Three, then select Parts Four and Five in your order of preference. Parts Four and Five are more important than Part Six, and therefore you should finish them before beginning Part Six.

PART ONE THE PROPERTIES OF CARBON

OBJECTIVES

When you have finished Part One, you will be expected to demonstrate acceptable performance on the following learning objectives:

- ✓1. Explain how the structure of the carbon atom permits the great number of organic compounds.
- ✓2. List at least ten uses of organic chemicals in your daily life.
3. Demonstrate that organic compounds contain carbon.
4. Trace carbon atoms through photosynthesis, and explain the carbon cycle.
5. Compare graphite and diamond in terms of their structures and properties.
6. Describe the formation of three fossil fuels.
7. Describe the chemistry of combustion, and explain why fuels are sources of energy.
8. Define activation energy, and describe the part it plays in the combustion of fuels.

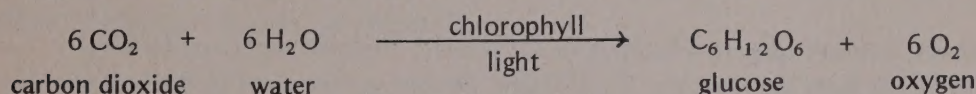
ORGANIC SECTION 1-1 CARBON: THE ELEMENT OF LIFE

Organic chemistry is the study of carbon compounds. You might wonder why so much attention is given to the study of just one element and its compounds. What's so important about carbon?

All living things contain carbon compounds. The building units of living matter—carbohydrates, proteins, and fats—are all carbon-containing compounds. All foods are organic compounds.

Photosynthesis

Carbon becomes a part of our foods, and eventually a part of our bodies, because of a unique chemical reaction that occurs in green plants. In the presence of light and a pigment called chlorophyll, green plants produce glucose, a sugar, from carbon dioxide (CO_2) and water. This reaction, in which oxygen is also produced, is called *photosynthesis*. In the reaction, light energy is converted to chemical energy. The general equation for photosynthesis is:



All living things depend on photosynthesis for their food. The sugar made by plants travels throughout the animal world as animals eat plants, and larger animals eat smaller ones. At each step, the sugar from photosynthesis is modified and combined with other materials. The resulting chemical compounds include new sugars, proteins, fats, starches, and cellulose.

Fossil Fuels

All living things eventually die. An organism dies when it can no longer sustain itself as an energy-using organization. The dead organism may become food for other organisms, or it may become trapped or buried in the earth. As a result of intense heat and pressure over long periods of time, some buried organic compounds have been converted into fossil fuels. Over millions of years, these organic deposits have formed peat, coal, and petroleum. Petroleum is not only a source of fuel, but also the starting material for the manufacture of plastics, fabrics, and industrial chemicals.

Probably every organic compound we know contains carbon that was once part of a living organism, or a product of a living organism. And because plants "recycle" carbon atoms from the atmosphere, a continuing source of organic compounds is available.

ORGANIC EXPERIMENT 1-1 EXTRACTING CARBON FROM ORGANIC COMPOUNDS

Purpose: To examine some properties of carbon and some of its compounds.

Materials

- | | |
|---------------------------------|-----------------------|
| 1 metal can or evaporating dish | cobalt chloride paper |
| 1 Pyrex beaker, 150 ml | 1 pair tongs |

Materials (continued)

1 asbestos pad	matchhead-size samples of each of the following:	
1 metal can lid	<i>p</i> -dichlorobenzene	paraffin
1 ringstand and ring	CaCO ₃	NaCl
1 candle	sucrose	mineral oil
150 g granulated table sugar	naphthalene	
20 ml concentrated H ₂ SO ₄		

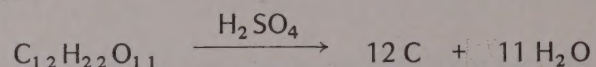
Procedure**PART I: CARBON FROM A CANDLE**

1. Light a candle and hold an object with a cool surface, such as a metal can lid, in the top part of the candle flame. In a few seconds, a black spot will appear on the surface. Move the lid back and forth. When the spot is 3–5 cm in diameter, blow out the candle. Let the lid cool.
2. When the lid is cool, touch the spot. Is the material on the spot sticky, or is it slippery? Does it come off the surface easily or is it strongly bonded to it? Record your observations. The material on the black spot is carbon in the form of soot. It results from the incomplete combustion of the candle wax. If the candle wax had been burned at high enough temperature and with sufficient oxygen, all the carbon in the candle would have been oxidized to carbon dioxide. By holding the metal lid in the flame, the temperature of the flame was lowered and incomplete combustion occurred. The result is the release of elemental carbon, some of which is deposited on the lid as a fine, soft, gritty-feeling powder.

PART II: CARBON FROM SUGAR

1. Place a layer of sugar, about 1 cm thick, in the bottom of the beaker after setting it on an asbestos pad. Pour about 20 ml of the sulfuric acid over the sugar. (Use enough acid to moisten all of the sugar.) Stand away from the beaker, and allow it to sit undisturbed. CAUTION: Concentrated H₂SO₄ can cause burns, so handle with great care. If any of it does get on your skin or clothes wash the area with large amounts of cold water and consult your teacher.
2. After several minutes, you will observe a reaction in the beaker. Describe what you observe. What odor do you detect from the reaction? CAUTION: Do not get too close to the beaker. The reaction you are observing releases heat and can be vigorous enough to spatter acid from the beaker.

The concentrated H₂SO₄ removes water from the sugar. A solid foam of elemental carbon with a caramel coating is formed. If the sugar were completely decomposed, the equation for the reaction would be:



The heat generated in the reaction vaporizes the water, causing the sugar and carbon to bubble up in the beaker. To show that water is present, use tongs to hold a piece of blue cobalt chloride paper in the fumes above the beaker. The paper turns pink in water vapor.

PART III: ORGANIC OR INORGANIC?

1. In a tin can lid, place a matchhead-size sample of each of the following materials: table sugar, *p*-dichlorobenzene (moth balls), and calcium carbonate. (See Figure 1–1.) Place the lid on an asbestos pad that you have set on a ringstand. Direct the tip of a Bunsen burner flame to each sample. What do you observe? Do all the samples burn? Do all leave deposits? If so, what color are the deposits? Record your observations.
2. Repeat this procedure with the following materials: naphthalene, paraffin, table salt, and 1 drop of mineral oil. Again record your results. The finely divided carbon that you observe in some of these reactions is used in printer's ink, black paint, shoe polish, carbon paper, and even automobile tires.

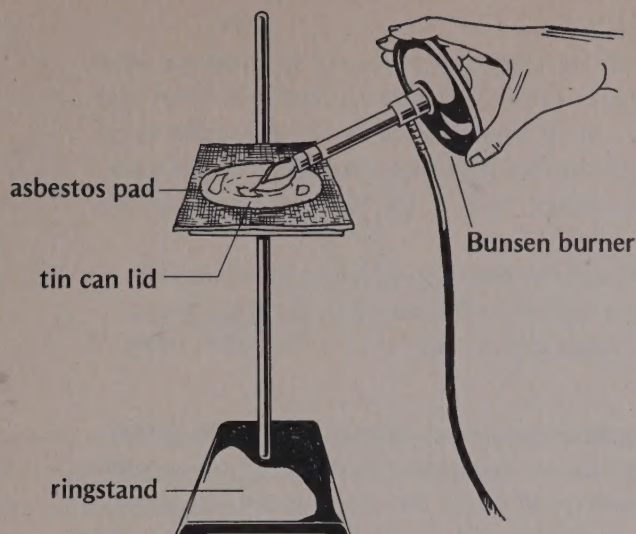


FIGURE 1-1: Laboratory setup for Experiment 1-1.

Questions

1. Make a list of the properties of the carbon observed in this experiment.
2. Make a list of the properties of the carbon compounds observed in this experiment.
3. Suggest ways to determine whether a substance is organic or inorganic.
4. Classify each of the following substances as organic or inorganic: paper, bread, glass, beeswax, cellophane, pepper, porcelain, paint, cardboard, silk, wood. What criteria did you use to classify each substance?

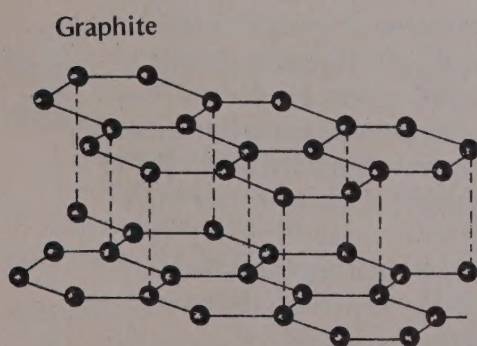
Suggestions for Further Study

Make a list of all the objects in your classroom which contain organic compounds. As a start, consider this book. Paper, made from trees, is certainly organic. Save your list. At the end of your study of organic chemistry, make another list. Compare the two lists to see if your recognition of organic materials has improved.

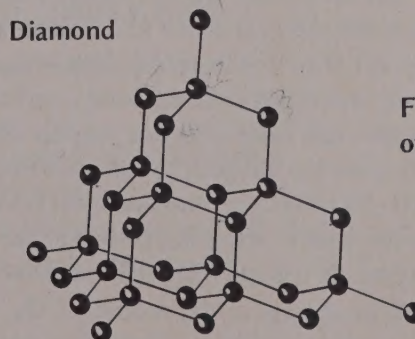
ORGANIC SECTION 1-2 USEFUL FORMS OF CARBON

Fossil fuels—peat, coal, petroleum—are the most frequently used natural forms of carbon. But there are also other forms of carbon whose unique properties are highly useful. For example, if you subject the fossil fuels, such as peat and coal, to intense heat and pressure, they will become a form of pure carbon called *graphite*. If you add even more heat and pressure, you may wind up with *diamond*, the hardest substance known.

Look at Figure 1-2. Compare the structures and properties of graphite and diamond. How do the structures of these substances determine their properties and uses?



Strong bonds hold the carbon atoms in each plane, but weaker forces exist between planes.



Strong bonds exist between all the carbon atoms. All the carbon atoms are equally spaced.

FIGURE 1-2: The structures of graphite and diamond.

Graphite: A Slippery Form of Carbon

Because the forces between the planes of graphite are weak, one plane can slip over the other. This makes graphite slippery and useful as a lubricant. Around the home, graphite is often used as a dry lubricant in locks. Its main use, however, is as an industrial lubricant. Because it keeps its properties at high temperatures, it is an ideal lubricant for high-speed machinery of all sizes. Graphite is also mixed with clay and baked to make pencil "lead." The higher the graphite content, the softer the lead.

Graphite is a good conductor of electricity. Because the electrons between the planes are loosely held (see Figure 1-2), they can flow easily under the influence of an electric current. Graphite is used to make electrodes for electric furnaces and arc lamps.

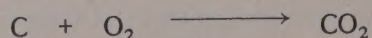
Diamond: The Hardest Substance Known

Diamond can scratch any other material, but nothing can scratch diamond. For this reason it is regarded as the hardest known substance. What causes diamond to be so hard? Like graphite, the carbon atoms in diamond are arranged in six-membered rings. But the rings are not arranged in planes. Instead, equally strong covalent bonds reach out in all directions, binding all the atoms in the crystal together. Unlike graphite, there are no weak bonds. Therefore, diamonds are not greasy, and they do not conduct electricity.

Because diamonds are so hard, they have many uses. Large diamonds, when cut and polished, are used as gems. Smaller, more abundant diamonds are used extensively for industrial grinding, cutting, polishing, and engraving processes. In addition to natural diamonds, which are mined mostly in South Africa and South America, diamonds can be made synthetically. To make a diamond, certain carbon compounds are subjected to extremely high temperatures and pressures. It is interesting to note that when organized as graphite, carbon atoms make an excellent lubricant. However, when organized as diamond, carbon atoms form a substance so hard that it can be used to grind and polish other materials. One function is literally the opposite of the other.

ORGANIC SECTION 1-3 THE CHEMISTRY OF BURNING

Carbon compounds, in the form of fossil fuels, are our main sources of energy. We use coal, oil, and natural gas to heat our homes, cook our food, and power our automobiles, trucks, and electric generators. How is energy obtained from organic compounds? The most common method used is burning.



Why does this burning process supply energy? Chemical changes involve the breaking and re-making of chemical bonds. Energy is required to break bonds; energy is given off when new bonds form. As fuels burn, the reorganization of bonds is exothermic—more energy is given off as the new bonds form than is consumed by breaking the old ones. (See *Keys to Chemistry*, page 47.)

Activation Energy

To burn coal or any other fuel, enough energy must be supplied to break the chemical bonds in both the oxygen molecules and in the fuel. Then, as carbon and oxygen form new bonds, more energy is given off than was invested. The *activation energy*, E_{act} , is the energy needed to cause collisions which will break existing bonds, and thus allow atoms to form new bonds. Two atoms or molecules that can react with one another often collide with energies too low to produce a reaction. This situation is analogous to two automobiles colliding when travelling at speeds of 2–4 km/h versus 10–20 km/h. In one case there is little or no damage. In the other case there is an *effective* collision—that is, there is significant damage.

The *heat of reaction*, ΔH , is the difference between the energy of the starting materials, C (coal) and O_2 , and the energy of the product, CO_2 . In this reaction, the product molecules have less energy than the starting materials. Therefore, energy is given off.

We know that to burn coal, it is necessary to supply enough energy to activate the reaction. This indicates that coal will not react with oxygen spontaneously. You know, for example, that a piece of coal in contact with air will not react unless a match or a burning piece of paper or

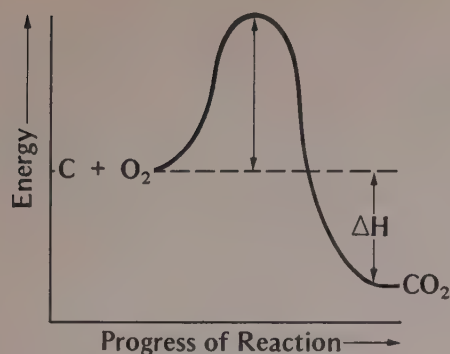


FIGURE 1-3: Potential energy diagram for the reaction $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$. The reaction is exothermic—the product, CO_2 , contains less total energy than the starting materials. What other exothermic reactions can you think of?

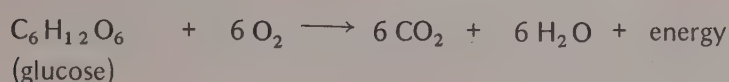
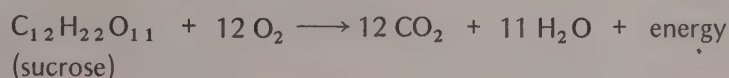
burning kindling is supplied. In fact, it's hard to start a coal fire. But once the coal begins to burn, the heat produced is more than enough to keep the reaction going. The fire supplies its own activation energy.

Combustion, a Form of Oxidation

All reactions in which carbon compounds burn are exothermic. The rapid oxidation of organic compounds in which energy is released as heat and light is called *combustion*. The heat produced in combustion reactions—that is, the heat of reaction—is called the *heat of combustion*. Complete combustion converts the carbon in organic compounds into CO_2 . Incomplete combustion results in the production of some elemental carbon (soot, ash) and carbon monoxide gas (CO). You are already familiar with two combustion reactions—the burning of candle wax and coal.

Oxidation in Living Organisms

In living organisms, the energy stored in the chemical bonds of certain organic compounds is released by oxidation. One of the quickest energy sources is sugar. Both table sugar (sucrose) and glucose (a natural sugar found in products such as honey and corn syrup) are oxidized in the human body:



The chemical equations for the complete oxidation of glucose and sucrose describe the *overall* changes through which energy is obtained from these sugars in living organisms. However, instead of being oxidized in one quick reaction, sugars are oxidized in a series of step-by-step reactions. By releasing energy in small steps, rather than in one big blaze, the energy in sugars can be used by organisms for building molecular structures and for supporting life processes.

✓ ORGANIC EXPERIMENT 1-2 DETERMINING THE HEAT OF COMBUSTION OF CANDLE WAX

Purpose: To measure the heat released by candle wax as it burns.

Materials

1 ringstand and ring	1 punch-type can opener
1 stirring rod	1 candle
1 metal can, ≈ 240 ml	1 balance, sensitive to 0.01 g
1 metal can, ≈ 960 ml	1 thermometer, -10°C to 110°C

Introduction

You know from Experiment 1-1 and from other experiences that a burning candle gives off energy as heat. But have you considered *how much* heat energy is given off?

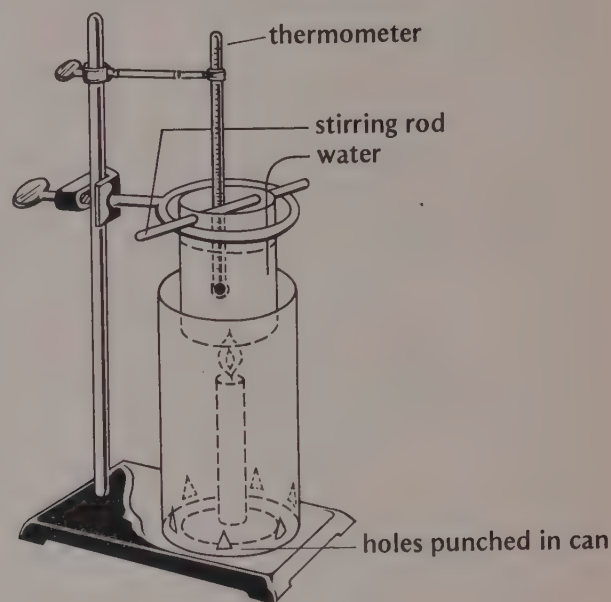
This experiment provides a crude technique to measure the heat released by burning candle wax. The heat given off is difficult to measure directly. If it is absorbed by something else,

however, it can be observed as a temperature change. The change in temperature that you will observe will be in a measured volume of water. However, you should realize that much of the heat produced in this experiment will be lost. Thus, the value you get will be a minimum value for the amount of heat released by the burning candle wax.

We express units of heat in *joules* (J). The amount of heat gained or lost by one gram of water as its temperature changes one degree Celsius is about 4.2 J. For example, if the burning candle wax releases enough heat to change the temperature of 100 g of water 30°C, then it has produced at least 12 600 J of heat (100 times 30 times 4.2).

On the basis of the above information, plan the procedure you will follow, and prepare a data table for the various measurements you will make to determine the heat of combustion of candle wax. As your end result, plan to obtain the minimum amount of heat contained in one gram of candle wax. Use Figure 1-4 as a source of ideas on how to use the equipment. Also, consider whether you are collecting the necessary data to answer the following questions.

FIGURE 1-4:
Laboratory setup for Experiment 1-2.



Questions

1. What mass of candle wax was burned?
2. What amount of water, in grams, was heated?
3. What temperature change occurred in the water?
4. How much heat, in joules, did the water absorb from the burning candle?
5. How much heat does the candle produce, as a minimum, for each gram that burns?
6. If candle wax has the formula $C_{25}H_{52}$, what is the heat of combustion per mole? Express your answer in joules per mole.

Suggestions for Further Study

1. Consider how you could redesign this experiment to get a better value for the heat of combustion of candle wax.
2. Calorimetry is the branch of chemistry devoted to determining the energy content of various foods and fuels. Try to find information about the equipment used to determine energy values, and compare that equipment with what you used for this experiment.
3. Use the *Handbook of Chemistry and Physics* and other sources to obtain values for the heat of combustion of various fuels and foods.

ORGANIC SECTION 1-4 THE BONDING PROPERTIES OF CARBON

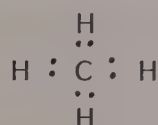
There are millions of organic compounds, and more are synthesized every day. The number of organic compounds far exceeds the number of all non-carbon compounds. The large number of organic compounds results from the ease with which carbon atoms bond with atoms of other elements and with each other.

Why does carbon bond so well? One reason is its tendency to bond by sharing electrons with other atoms, rather than losing or gaining electrons to form ions. In other words, carbon atoms form *covalent bonds*. (For a review of covalent bonding, see *Keys to Chemistry*, page 189, “The Covalent Bond.”) The covalent bonds that carbon forms with other carbon atoms tend to be quite stable.

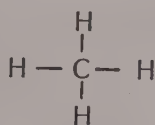
Carbon has four electrons and four orbitals in the valence energy level. This means that each carbon atom can form four covalent bonds with other atoms. Each of these bonds contains two electrons. Usually one electron is contributed by each atom that is bonded.

ORGANIC SECTION 1–5 FORMULAS FOR CARBON COMPOUNDS

A number of methods have been devised to represent molecules and to show the chemical bonds in compounds. One is an *electron-dot* notation, in which a bond and its pair of electrons is represented by a pair of dots. Figure 1–5 shows the electron-dot formula for methane. In a simpler representation the pair of dots is replaced by a short line. The new representation is called a *structural formula*. In a structural formula, the short line between two atoms represents a pair of shared electrons. Molecules may also be represented by a *molecular formula*. However, the molecular formula shows only the numbers and kinds of atoms in a compound; it does not show how the atoms are arranged. In organic chemistry, the structural formula is most useful.



electron dot
formula



structural
formula



molecular
formula

FIGURE 1–5: Three different ways to represent the compound methane.

Sometimes a structural formula and a molecular formula are blended into a hybrid called a *condensed formula*. A condensed formula may be used to simplify the representation of complex molecules. Table 1–1 provides a few examples of molecular, structural, and condensed formulas. The electron-dot formulas are used as learning devices and for a careful analysis of the bonding in a compound. They are not used as a general way to represent compounds.

Table 1–1: Some Examples of Molecular, Structural, and Condensed Formulas

Name of Compound	Molecular Formula	Structural Formula	Condensed Formula
Ethane	C_2H_6	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H} - \text{C} - \text{C} - \text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	CH_3CH_3
Propane	C_3H_8	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H} - \text{C} - \text{C} - \text{C} - \text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\text{CH}_3\text{CH}_2\text{CH}_3$
Pentane	C_5H_{12}	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \\ \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \\ \quad \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$

Although structural formulas are handy ways to represent compounds, they are not ideal representations. The reason is that molecules are three dimensional, and formulas are only two dimensional. The best way to develop insight about the three-dimensional nature of organic molecules is to build models. It will help you to see the versatility of the carbon atom, and to understand why carbon can serve as a backbone for so many compounds.

ORGANIC EXPERIMENT 1-3 MODEL BUILDING: METHANE

Purpose: To construct a model of the methane molecule.

Materials

4 small white Styrofoam spheres
1 large black Styrofoam sphere
toothpicks

2 rubber bands
1 protractor
modeling clay

Procedure

1. Join two white Styrofoam balls with a rubber band. Pull them apart slightly, then let them snap back together by holding one sphere and letting go of the other.

FIGURE 1-6



The spheres attract each other (the rubber band is responsible for this), but they also repel each other. They are pulled together by the rubber band; but when they touch each other, they stop moving: the repelling forces prevent them from getting closer. Assume that the two white spheres represent two atoms surrounded by their electrons, and that the outer surface of each sphere represents the outer surface of the electron region. The atoms attract each other until they reach a certain point; then a repulsive force sets in and opposes the attraction.

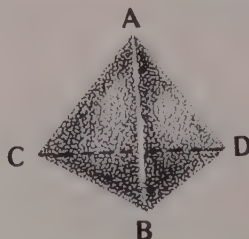
2. Take a second pair of white spheres and join them with a rubber band. Separate the spheres slightly and slip them over the first set of spheres so that the rubber bands cross each other. Carefully allow the spheres to stop moving. Note how the four spheres are arranged when they come to rest. (See Figure 1-7.)

FIGURE 1-7



If you look closely, you will see that the four spheres form the corners of a regular tetrahedron. (A regular tetrahedron is a four-sided figure, each side of which is an equilateral triangle.) The tetrahedral arrangement is the most stable arrangement for four like objects around a single point. (See Figure 1-8.) The four hydrogen atoms in methane occupy the corners of a tetrahedron. The center of the tetrahedron is occupied by a carbon atom.

FIGURE 1-8



3. To get a better feel for the tetrahedral shape, construct a tetrahedron. Use six toothpicks to represent the edges of the tetrahedron; use four small clay spheres to form the corners. (See Figure 1-9.) Examine the tetrahedron. Note that there are four vertices and four sides; each side is an equilateral triangle. Using toothpicks, build a model of methane by attaching four small white Styrofoam balls (representing hydrogen) to a larger black Styrofoam ball that represents carbon. The hydrogens should be placed around the carbon so that they form the corners of a regular tetrahedron; the carbon should be at the center of the tetrahedron. The H-C-H angle in each case is about 109° , the tetrahedral angle. Using a protractor,

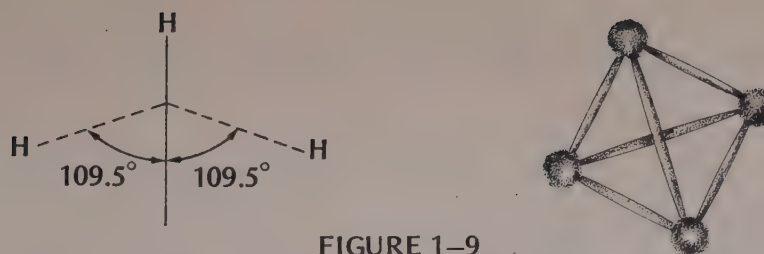


FIGURE 1-9

roughly measure the H—C—H angles in your model. Are they close to the angles found in the theoretical model? If not, modify the angles accordingly.

SUMMARY, PART ONE

Organic chemistry is the study of the carbon atom and its compounds. Because of its ability to form covalent bonds, the carbon atom bonds readily with other atoms, forming a great array of stable compounds. Carbon compounds, in the form of fossil fuels, are our main sources of energy. Fossil fuels contain energy captured by photosynthesis and stored in organic molecules. This energy can be released by combustion or oxidation. In Part Two, some further properties of carbon and carbon compounds will be investigated.

SUGGESTIONS FOR FURTHER STUDY

1. Diamond is the hardest known substance. How, then, does a diamond cutter cut diamonds? Does he really cut them?
2. Photosynthesis is a complex chemical process. Since it is the source of energy for all life, you may want to research its intricacies. Consult the bibliography of Part One for references for your research.
3. During photosynthesis, the energy of the sun is used to build glucose molecules. Plants and animals subsequently break down glucose molecules to obtain energy for various life processes. The process of obtaining energy from the bonds of the glucose molecules is called *respiration*. Respiration occurs in a number of steps, usually referred to as the *citric acid cycle*. You might wish to research what happens in this cycle.

BIBLIOGRAPHY

Anon., "Organic Matter in the Environment," *Chemistry*, March, 1973, p. 22.

Discusses the role of water animals and microorganisms in metabolizing oils (e.g. oil spills), proteins and metals. Also discusses how they modify the carbon cycle, and suggests how they might control pollution.

Bundy, Francis P., "Superhard Materials," *Scientific American*, August, 1974, p. 62.

The hardness of several materials is compared to diamond in terms of the strength and orientation of the bonds between atoms. Synthetic materials can be made hard, but the hardest of these (cubic boron nitride) is only half as hard as diamond. Hardness is defined in terms of the chemistry and geometry of crystal structure.

Govindjee and Govindjee, Rajni, "The Primary Events of Photosynthesis," *Scientific American*, December, 1974, p. 68.

The absorption of light by the chlorophyll pigment molecule and the transmission of its energy to other molecules are explained in terms of electron flow, excitation energy, fluorescence, etc. Excellent photographs of the chloroplast.

Szabadvary, Ferene, "Birth of Organic Chemistry," *Chemistry*, December, 1973, p. 13.

Describes some of the events that made people realize that carbon compounds could be made synthetically. Describes how the synthesis of aniline dye from coal tar started the gigantic organic chemical revolution.

PART TWO ORGANIC COMPOUNDS: THEIR STRUCTURES AND PROPERTIES

OBJECTIVES

When you have finished Part Two, you will be expected to demonstrate acceptable performance on the following learning objectives:

1. Describe the relationship between the structures and properties of molecules, using methane, methanol, and water as your examples.
2. Build structural models of ethane, propane, ethylene, and acetylene.
3. Write molecular formulas, structural formulas, and condensed formulas for complex molecules.
4. Predict the boiling point sequence of compounds in the alkane series.
5. Explain the meaning of the term *octane rating* as it is used to describe gasoline.
6. Draw formulas for some structural isomers.
7. Describe straight-chain, branched-chain, ring, and aromatic compounds.
8. Explain why unsaturated hydrocarbons are more reactive than saturated hydrocarbons.
9. Define the term *fractional distillation*, and explain how it can be used for separating mixtures of liquids.
10. Explain "strain" in relation to bond angles.
11. Describe the structure of benzene.
12. Compare the reactivity of saturated and unsaturated hydrocarbons.
13. Write equations showing the reaction of bromine with saturated and unsaturated hydrocarbons.

ORGANIC SECTION 2-1 PROPERTIES OF SIMILAR ORGANIC COMPOUNDS

Methane is the simplest organic compound. It is the major constituent (90%) of natural gas, which is used in most home stoves. The odor you smell when there is a gas leak, or when the pilot light goes out, is not that of methane, which is odorless. For safety reasons, a small amount of a strong-smelling gas is added to natural gas so that leaks can be detected easily.

Methane is highly flammable. What happens to this and other properties if we change any of the atoms of the methane molecule? Table 2-1 shows some physical properties of three compounds—methane, methanol, and water. Using the table, compare the structure and properties of methane with those of methanol and water. What similarities and differences do you find? How important does molecular mass appear to be in determining the properties of these molecules? What part of the methanol molecule, do you think, determines its solubility in water?

Table 2-1: Some Properties of Methane, Methanol, and Water

	Methane CH ₄	Methanol CH ₃ OH	Water H ₂ O
Molecular formula	CH ₄	CH ₃ OH	H ₂ O
Structural formula	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{H} \quad \text{H} \end{array}$
Molecular mass	16	32	18
Physical state (at room temp.)	Gas	Liquid	Liquid
Melting Point °C	-182.5	-98	0
Boiling Point °C	-161.5	65	100
Solubility in water	slight	100%	100%
Flammable	yes	yes	no
Density	0.72 g/l at 0°C	0.79 g/ml	1.00 g/ml

On the basis of your analysis of methane, methanol, and water, would you conclude that the *kinds of atoms* determine the properties of molecules? Explain.

EXPERIMENT 2-1 PHYSICAL PROPERTIES OF SOME ORGANIC COMPOUNDS

In this activity, you will examine the properties of some organic compounds with low molecular masses. The compounds are *ethanol* (ethyl alcohol), *chloroform* (an organic solvent), *benzene* (another solvent and a major starting compound for the synthesis of many organic compounds), and *carbon tetrachloride* (a solvent which has been used extensively for dry cleaning). Except for ethanol, all of the compounds you will use in this activity are pure substances; they are not solutions. Ethanol normally contains 5% water and often, also, contains small amounts of chemicals that render it unfit for use in beverages.

Purpose: To examine the properties of some organic compounds of low molecular mass.

Materials

Handbook of Chemistry and Physics

Procedure

1. Prepare a table like the one shown.

Data Table, Experiment 2-1

	<u>Ethanol</u>	<u>Chloroform</u>	<u>Benzene</u>	<u>Carbon tetrachloride</u>
Molecular formula				
Structural formula				
Molecular mass				
Physical state (at room temp.)				
Melting Point °C				
Boiling Point °C				
Solubility in water				
Density				

2. Your teacher will prepare a display of the four compounds in sealed containers which you can examine to determine the physical state of each at room temperature.
3. Look up the four compounds in the *Handbook of Chemistry and Physics*. Use any other references you need to complete the table.

Suggestions for Further Study

Suggest a way to determine the density of a compound that is soluble in water. As a reference, consult the *Laboratory Manual for Keys to Chemistry*, Experiments 1-3 and 1-4.

ORGANIC SECTION 2-2 HYDROCARBONS

One of the simplest groups of organic compounds are the *hydrocarbons*—substances that contain only carbon and hydrogen. We've already discussed methane, the simplest hydrocarbon molecule. Often we refer to *saturated* hydrocarbons. A saturated hydrocarbon is one that is "filled up." This means that each carbon atom is connected to hydrogen atoms or other carbons by single bonds (sharing only two electrons). In all saturated carbon compounds, the carbon bonds are single bonds.

Saturated Hydrocarbons: Alkanes

Saturated hydrocarbons, or *alkanes*, form a series of compounds that differ from each other by only a $-\text{CH}_2$ unit. Compounds that differ from each other by this unit are called *homologs*. Methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) are homologs. They are the first members of the homologous series of alkanes. The next homolog in the series is called butane. Alkanes all have names ending in *-ane*, and the general formula $\text{C}_n\text{H}_{2n+2}$.

Propane and butane are often used as fuels in camping equipment, and in stoves and furnaces in rural homes. Both propane and butane can be converted into liquids. Of what advantage might it be to ship a compound as a liquid rather than a gas?

Some Practice Problems Involving Alkanes

1. Write structural formulas for ethane, propane, and butane.
2. Predict what will happen to the boiling points, melting points, and water solubilities of alkanes as the molecular masses increase. Check your predictions by referring to Table 2-2.

Table 2-2: Physical Properties of Some Larger Alkanes

Alkane	Molecular Formula	Melting Point °C	Boiling Point °C	Solubility in Water
Hexane	C_6H_{14}	-94.3	68.7	negligible
Octane	C_8H_{18}	-56.5	125.7	negligible
Octadecane	$\text{C}_{18}\text{H}_{38}$	28.2	306.0	insoluble

ORGANIC EXPERIMENT 2-2 MODEL BUILDING: ETHANE AND PROPANE

In Experiment 1-3, you built a three-dimensional model of the methane molecule. In this experiment, you will build models for homologs of methane.

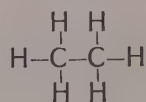
Purpose: To construct molecular models of ethane and propane.

Materials

- 3 large black Styrofoam spheres
- 8 small white Styrofoam spheres
- toothpicks

Procedure**PART I: BUILDING A MODEL OF ETHANE**

Build a model of the ethane molecule. First, look at the structural formula for ethane:



ethane

Start building the model by joining two black Styrofoam spheres (carbon atoms) with a toothpick. Next, attach three hydrogen spheres to each carbon sphere. Remember that the four atoms around each carbon atom should be situated at the corners of a tetrahedron.

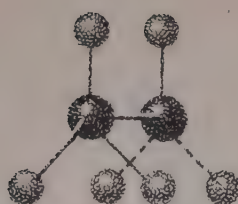


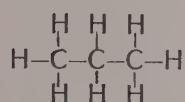
FIGURE 2-1:
Ball-and-stick model of ethane.

Questions

What happens to the structure of ethane when you rotate some of its atoms? Rotate a hydrogen on the bond that attaches it to a carbon atom. Then rotate one of the carbon atoms on the bond that joins them. In which case is there an apparent change in the structure? (Note: *Rotational isomers* are different arrangements of atoms that can be converted into one another by *rotation* about single bonds. These isomers cannot be isolated from one another because they change back and forth from one form to another so rapidly. You can't for example, place one rotational isomer of ethane in a bottle and keep it from becoming all the other rotational isomers. In Organic Section 2-3, we will look at some *structural isomers*—compounds that have the same molecular formula but cannot be interconverted readily.)

PART II: BUILDING A MODEL OF PROPANE

Starting with your ethane model, build a model of propane. First, look at the structural formula of propane:



propane

Remove one of the hydrogen atoms from the ethane model, leaving the toothpick (the bond) in place. Replace the hydrogen atom with a carbon. Notice that all the hydrogens in ethane are equivalent, so it makes no difference which one you replace. Next, attach three hydrogen spheres to the new carbon. Remember that the four atoms around each carbon should be situated at the corners of a tetrahedron.

Questions

Are the eight hydrogens of propane equivalent? Rotate one of the end carbons around the bond attaching it to the central carbon. Is there a change in the spatial relationship of the atoms?



FIGURE 2-2:
Ball-and-stick model of propane.

Suggestion for Further Study

The most stable rotational isomers of a compound are those with the greatest separation between atoms not bonded to each other. Using your models, try to find the most stable rotational isomers of ethane and propane. Watch the change in the distance between two hydrogen atoms bonded to different carbon atoms, as you rotate one of the carbon atoms.

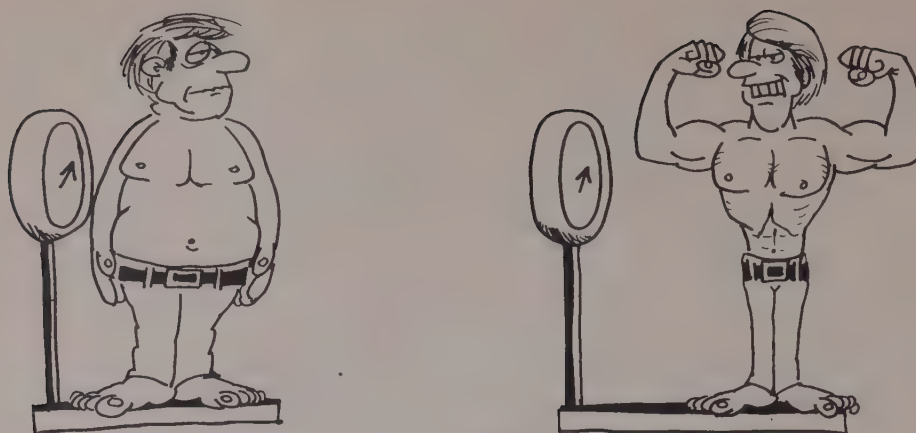


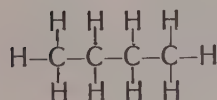
FIGURE 2-3

IT'S NOT WHAT YOU'VE GOT,
BUT HOW IT'S ARRANGED THAT COUNTS!

ORGANIC SECTION 2-3

STRUCTURAL ISOMERS: THE SAME ATOMS IN DIFFERENT ARRANGEMENTS

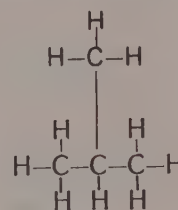
Many carbon compounds are made up of straight chains of carbon atoms. However, branched chains are very common. For example, a compound with molecular formula C_4H_{10} might have either of the following structures:



butane
(or *n*-butane)

Melting point $-138^{\circ}C$
Boiling point $-0.5^{\circ}C$

or



isobutane

Melting point $-159^{\circ}C$
Boiling point $-12^{\circ}C$

Notice that butane is also called *n*-butane. The prefix *n*- (an abbreviation for *normal*) is sometimes used in naming straight-chain alkanes and other compounds derived from them. Prefixes such as *iso*- and *neo*- are used with other isomers to distinguish them from the straight-chain isomer.

Note that isobutane has the same molecular formula, C_4H_{10} , as butane. However, because the atoms are arranged differently, the compounds differ in some physical properties, for example, melting points and boiling points. Compounds having the same molecular formula but different structures are called *structural isomers*.

Two Isomer Problems

1. There are three structural isomers of pentane, C_5H_{12} . One is shown in Table 1-1. Draw structural formulas for the other two.
2. If you can collect enough Styrofoam spheres, make models of each of the structural isomers of pentane.

ORGANIC EXPERIMENT 2-3

DETERMINING THE BOILING POINTS OF SEVERAL SATURATED HYDROCARBONS

Purpose: To demonstrate a method for determining the boiling points of liquids, and to show the effect of branching on the boiling points of compounds whose molecular masses are similar.

Materials

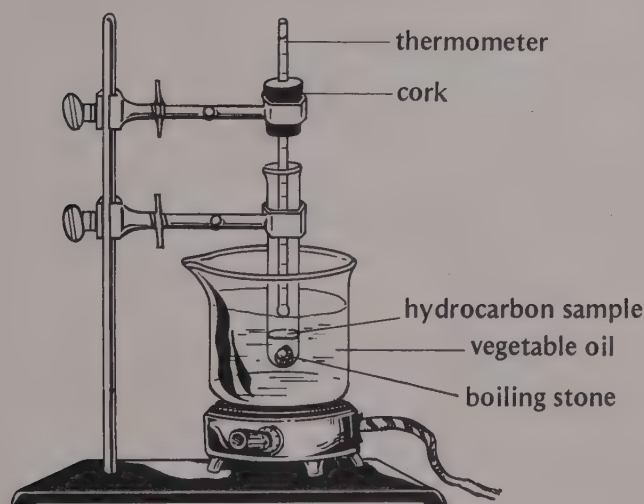
1 thermometer, -20°C to 150°C	boiling stones	
1 ringstand and ring	50 ml vegetable oil for each oil bath	
2 test tube clamps	5 ml of each of the following hydrocarbons:	
1 watch glass	hexane	3-methylhexane
tongs	heptane	2, 4-dimethylpentane
1 hot plate or Bunsen burner	octane	2, 2, 4-trimethylpentane
beakers, 100 ml for each oil bath		(isooctane)
5 test tubes, 18 mm x 150 mm		

CAUTION: Since hydrocarbons are extremely flammable, be very careful to put the dispensing bottle away before lighting a burner. Also, work with only one hydrocarbon at a time. Keep the flame as low as possible; the hydrocarbon vapors are also flammable. If the sample does catch fire, merely lift the thermometer out of the test tube and cover the tube with a watch glass to smother the flame. If the vegetable oil catches fire, smother it by covering the beaker with a watch glass after lifting the test tube assembly out of the way.

Procedure

1. Set up the apparatus as shown in Figure 2-4. The thermometer should be inserted into a cork stopper with a hole that holds the thermometer firmly, yet allows easy adjustment up and down. Use a burner only if a hot plate is not available.
2. Place about 50 ml of vegetable oil in the beaker and 5 ml of sample hydrocarbon and a boiling stone in the test tube. Adjust the thermometer so that the end of the bulb is about one cm above the surface of the hydrocarbon sample. Immerse the test tube in the vegetable oil so that all of the sample is below the level of the oil.

FIGURE 2-4: Laboratory setup for Experiment 2-3.



3. Heat the beaker of vegetable oil gently so that its temperature rises quite slowly. Watch the hydrocarbon sample, and *when it just starts to boil, turn off the heat*. Read the temperature while the liquid is boiling, and record it.
4. Remove the thermometer; wipe it clean and put it in a safe place. Using tongs, lift the test tube out of the oil, allowing any surface oil to drip from it. Wipe off the remaining oil, then run cold water over the outside of the test tube. Once it is cool, pour the hydrocarbon sample into a container designated by your teacher.
5. If you are going to do more than one boiling point determination as your share of the data collection process, it is best to use a fresh beaker of oil since the first one will be quite hot. Once cool it can be used again. Also use a clean test tube. Repeat steps 2, 3, and 4 for as many hydrocarbon samples as you elect to do.

Questions

1. How do the boiling points of the compounds with the straight-chain molecules compare with those of the compounds with branched molecules?
2. Based on this experiment, what tentative conclusions can you draw about the effect of branching on the boiling points of compounds?
3. Optional: If you are so inclined and can round up the necessary Styrofoam spheres, build models of these molecules.

ORGANIC SECTION 2-4 UNSATURATED ORGANIC COMPOUNDS

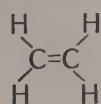
So far we have discussed only organic compounds in which all of the bonds between neighboring atoms are single bonds—bonds consisting of a single pair of shared electrons. Single bonds are stable and relatively unreactive. However, many organic molecules exist with double and triple bonds between carbon atoms. Double bonds arise when two pairs of electrons are shared between two atoms. Triple bonds are formed when two atoms share three pairs of electrons.

Although it is harder to break *both* bonds of a double bond than to break a single bond, it is much easier to break one of the bonds in a double bond than it is to break a single bond. As a result, unsaturated compounds tend to be more reactive than saturated compounds.

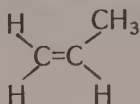
Hydrocarbons with Double Bonds: Alkenes

Hydrocarbons with double bonds are called *alkenes*. They all have names ending in *-ene*.

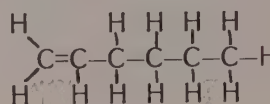
Here are structural formulas for a few alkenes:



ethylene



propylene



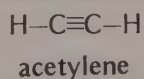
1-hexene

Ethylene, the simplest alkene, is an important industrial chemical. A large portion of the ethylene produced annually is used as a starting material in the manufacture of polyethylene, which is used to make plastic squeeze bottles, sandwich bags, and wrapping materials. Ethylene is also used to make ethylene glycol, a major component of the antifreeze used in car radiators.

The three-carbon alkene, propylene, is the starting material in the manufacture of polypropylene, which is used for fibers, plastic pipes, plastic sheets, and plastic bottles.

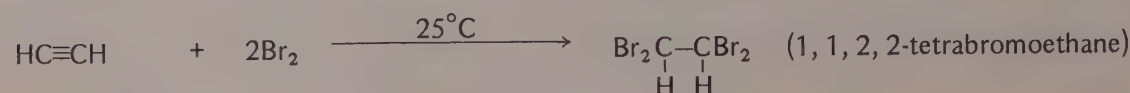
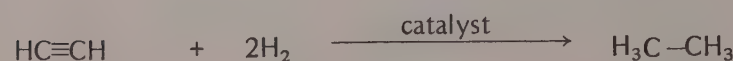
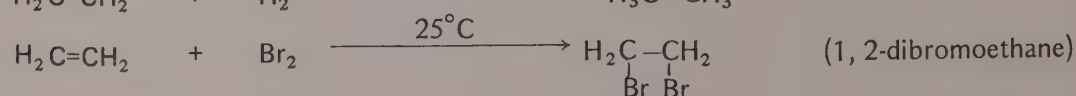
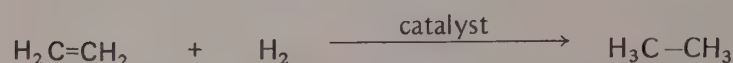
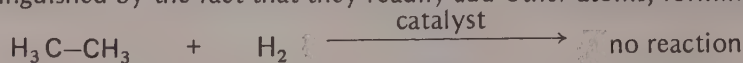
Hydrocarbons with Triple Bonds: Alkynes

Hydrocarbons containing triple bonds are called *alkynes*. The simplest alkyne is acetylene, C_2H_2 :



Acetylene is used as a fuel in oxy-acetylene welding torches. It is also the starting material in the industrial preparation of several plastics and acetic acid (vinegar).

Alkenes and alkynes are called unsaturated because there are multiple bonds between carbons—that is, not all of the carbons are saturated with hydrogen. The unsaturated hydrocarbons are distinguished by the fact that they readily *add* other atoms, forming saturated compounds.



ORGANIC EXPERIMENT 2-4 MODEL BUILDING: ETHYLENE AND ACETYLENE

Purpose: To explore the effects of double and triple bonds on rotation and on the geometry of molecules.

Materials

- 2 large black Styrofoam spheres
- 4 small white Styrofoam spheres
- toothpicks

PART I: BUILDING A MODEL OF ETHYLENE, C_2H_4

1. First connect two black carbon spheres together, using two toothpicks to represent the double bond. Note that having two toothpicks between the spheres eliminates the free rotation that existed when only one toothpick connected the two spheres.
2. Now attach two hydrogens to one of the carbons. There will only be three atoms attached to this carbon—two hydrogen atoms and another carbon atom. You should maximize the angular distance between these three atoms. What should the $H-C-H$ angle be to meet this condition?
3. Complete the model by attaching the last two hydrogens to the second carbon. (See Figure 2-5.) Use the same bond angles used in attaching the hydrogens to the other carbon atom—but with the added condition that these hydrogen atoms must be in the same plane as all the other atoms. All six atoms of the ethylene molecule should lie in the same plane.

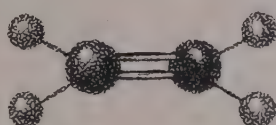


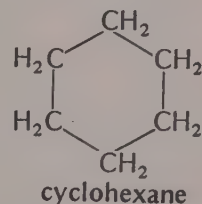
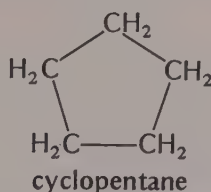
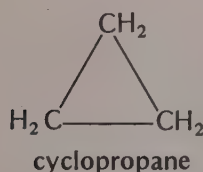
FIGURE 2-5: Ball-and-stick model of ethylene.

PART II: BUILDING A MODEL OF ACETYLENE, C_2H_2

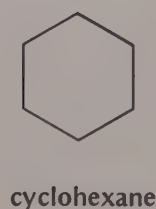
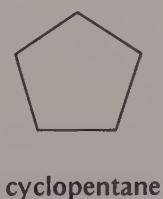
1. Attach two carbon spheres, using three toothpicks. Again note the restriction on rotation that accompanies multiple bonding between atoms.
2. Now attach a hydrogen to one of the carbon spheres. Each carbon sphere will be attached to only two other atoms—one carbon and one hydrogen. You should maximize the angular distance between the carbon and hydrogen. What should the $C\equiv C-H$ bond angle be to meet this condition?
3. Attach the other hydrogen sphere to the second carbon in exactly the same way. Describe how the four atoms are spatially related in the acetylene molecule.

ORGANIC SECTION 2-5 RING COMPOUNDS

Carbon atoms bond not only in straight and branched chains, but in rings (closed chains) too. Some of the simpler ring compounds are:



The structure of ring compounds can be shown by a kind of shorthand. For example, the three compounds shown above can also be shown as follows:



How does the ring structure affect the properties of these molecules? The three carbon atoms of cyclopropane really have to strain in sharing electrons with each other. The normal bond angle between carbon atoms in saturated hydrocarbons is about 109° . What is the bond angle in cyclopropane? (You might think of a fat person trying to tie his shoelace.) This "ring strain" causes cyclopropane to be very reactive compared with other hydrocarbons; the ring opens readily. In contrast, in cyclopentane and cyclohexane the bond angles between the carbon atoms do not produce strain, and therefore these compounds are much less reactive.

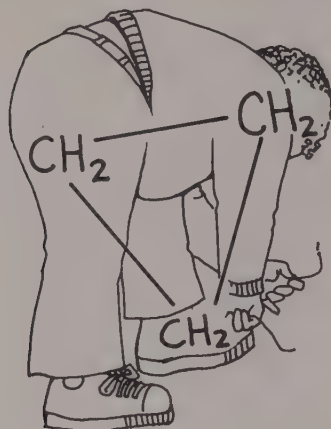
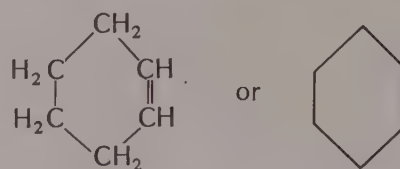


FIGURE 1-6:

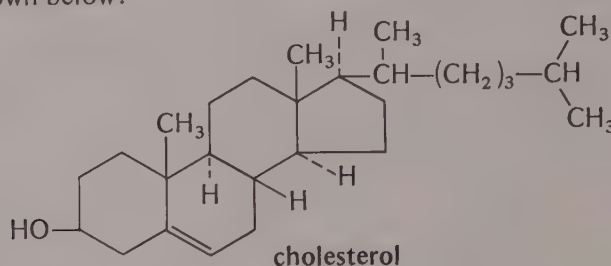
An overweight person may have trouble bending over to tie a shoe. Similarly, the three carbon atoms in cyclopropane are strained by sharing electrons with each other. How does this affect the reactivity of cyclopropane?

So far, all of the ring compounds that we discussed have been saturated, but unsaturated rings also exist. Cyclohexene is an example.



cyclohexene

Cholesterol, whose molecular formula is $C_{27}H_{45}OH$, is the compound most often connected with hardening of the arteries. It also is the major constituent of gallstones. Cholesterol contains several rings. Identify cyclohexane, cyclohexene, and cyclopentane in the condensed formula for cholesterol shown below:

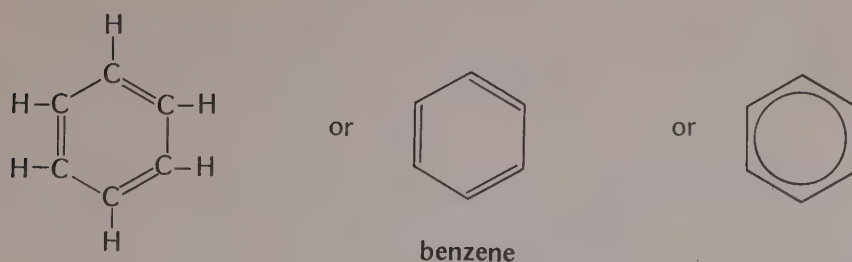


The Benzene Ring and Aromatic Compounds

Aromatic compounds, of which there are thousands, are formed from benzene and benzene derivatives. The principal source of benzene is coal tar. Aromatic compounds were first named because of the fragrance of many of their derivatives. Some aromatics smell very sweet; others smell very bad. Many aromatic compounds are hazardous to health and some have been associated with cancer-causing materials. For this reason care should be exercised in handling these compounds; especially avoid breathing the vapors.

The molecular formula for benzene is C_6H_6 . The six carbon atoms form a ring. A single hydrogen atom is attached to each carbon. We frequently write a structural formula for benzene

which shows three double bonds. Benzene's real structure, however, is a little more complicated and not easy to describe precisely. The modern representation for benzene is a hexagon with a circle inscribed.



ORGANIC EXPERIMENT 2-5

COMPARING THE REACTIVITY
OF SATURATED AND UNSATURATED HYDROCARBONS

Purpose: To compare the reactivity of saturated and unsaturated chain and ring hydrocarbons.

Materials

12 test tubes, 13 mm x 100 mm

2 test tube racks

marking pencil or labels

12 stoppers for test tubes

solution of 0.1M KMnO_4 in 1M H_2SO_4

1 glass stirring rod

solution of 0.1M Br_2 in CCl_4

2 ml of each of the following:

hexane

cyclohexene

1-hexene

benzene

cyclohexane

toluene

Introduction

In order to know whether a chemical reaction has occurred, an observable change must be evident. All of the hydrocarbons we will use in this experiment are clear liquids, and any reactions they undergo may produce new clear liquids. Therefore, to determine whether the compounds do undergo a chemical change, we must allow them to react with something which will cause a *visible* change. Two such substances are bromine, Br_2 , and permanganate ion, MnO_4^- . Bromine in carbon tetrachloride has a strong yellow-red color. When the bromine reacts, this color fades and disappears. The color of permanganate ion in water is a deep purplish-red. The color can be changed by reduction to green, brown, or clear, since manganese has a number of oxidation states. In this experiment, color changes are evidence of reaction.

CAUTION: Since hydrocarbons are extremely flammable, stay away from any open flame as you do this experiment. Also work in a well ventilated area, preferably under a fume hood, and avoid breathing the fumes from these compounds.

Procedure

1. Prepare a table in which you can record your observations. Since some of the reactions may proceed slowly, your table should enable you to record an observation after 1 min and again after 5 min. Also, remember that you will be observing twelve different test tubes and their contents. This means that you will have to keep track of what is in each one.
2. Add 1 ml of each hydrocarbon to six test tubes. To each hydrocarbon sample, add permanganate solution drop by drop, stirring the sample after each drop is added. Count the number of drops you add, and record any color changes you observe. After how many drops does the permanganate color persist after stirring? Record.
3. Set up six test tubes so that each contains about 1 ml of a different hydrocarbon. Add a drop of bromine solution to each one of the tubes and stir. Then add another drop of bromine solution to each tube and stir. Continue until you have added 20 drops (1 ml) to each tube. Continue adding drops of bromine to any tube in which the bromine color has been disappearing until the color stops disappearing.

Questions

1. Write the structural formulas for the hydrocarbons that you tested.
2. Which of the hydrocarbons reacted readily with MnO_4^- ? What relationship do you find between reactivity and structure?
3. Which of the hydrocarbons reacted readily with the bromine solution? What relationship do you find between reactivity and structure?
4. Write equations to show the reaction (if any) of bromine (Br_2) with hexane, 1-hexene, and cyclohexene.

ORGANIC SECTION 2-6 CRUDE OIL AND FRACTIONAL DISTILLATION

When pumped from underground wells, crude oil is composed of a variety of straight-chain, branched-chain, and cyclic saturated hydrocarbons, as well as with some aromatic hydrocarbons. These compounds range in complexity from methane, CH_4 , to components of heavy oil containing 70–80 carbon atoms.

Crude oil is divided into fractions in a process called fractional distillation. *Distillation* is the process of vaporizing a liquid and then condensing the vapor. *Fractional distillation* is used to separate the components of a liquid mixture by taking advantage of differences in the boiling points of the components. In oil refineries the crude oil is heated to over 400°C , and most of the hydrocarbons are vaporized. The hot vapors are passed into the bottom of a tall fractionating tower. The tower is divided into various levels like the floors of a tall building. The levels at the bottom are hottest; those at the top are much cooler. The lowest boiling hydrocarbons, the gases, rise to the top of the tower, where they are cooled and collected. The gasoline fraction rises close to the top and is collected. The kerosene fraction is collected below that, and so on, until the asphalt fraction is collected toward the bottom. (See Figure 2-7.)

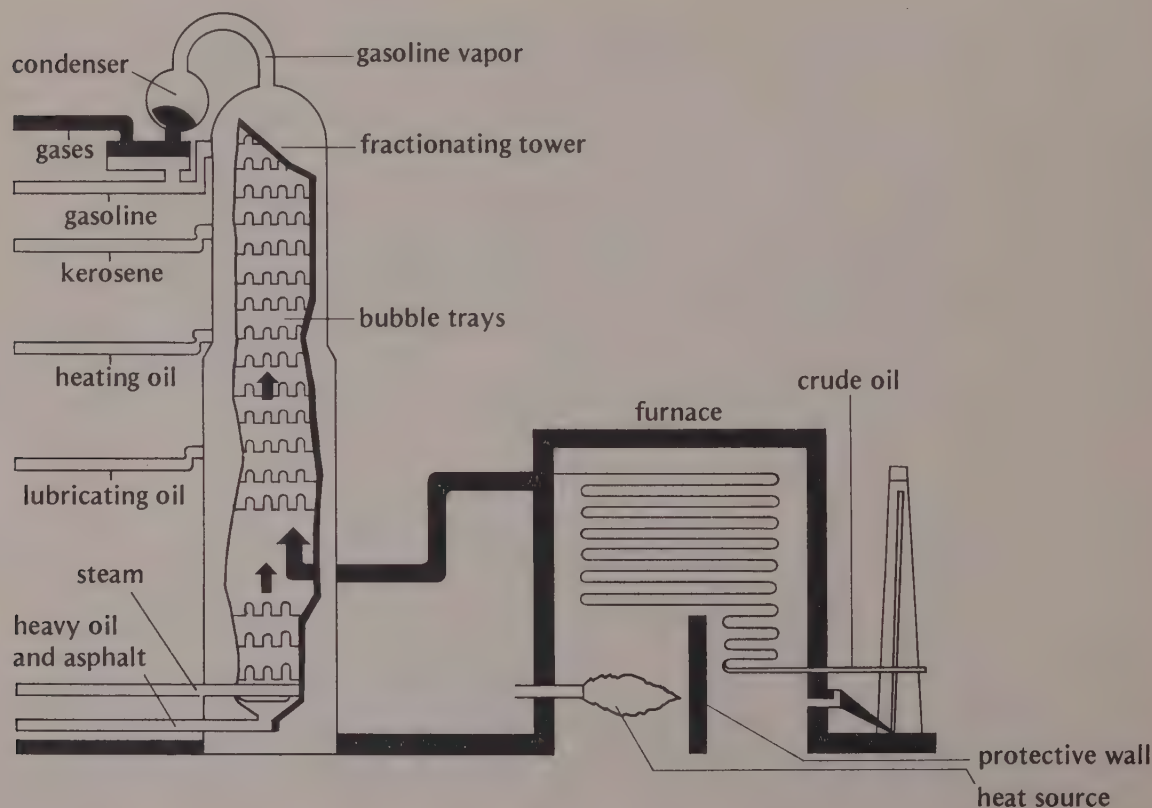


FIGURE 2-7: The components of crude oil are separated in a fractionating tower. During refinement, the components with the lowest boiling points rise toward the top of the tower. Those with high boiling points remain at the bottom.

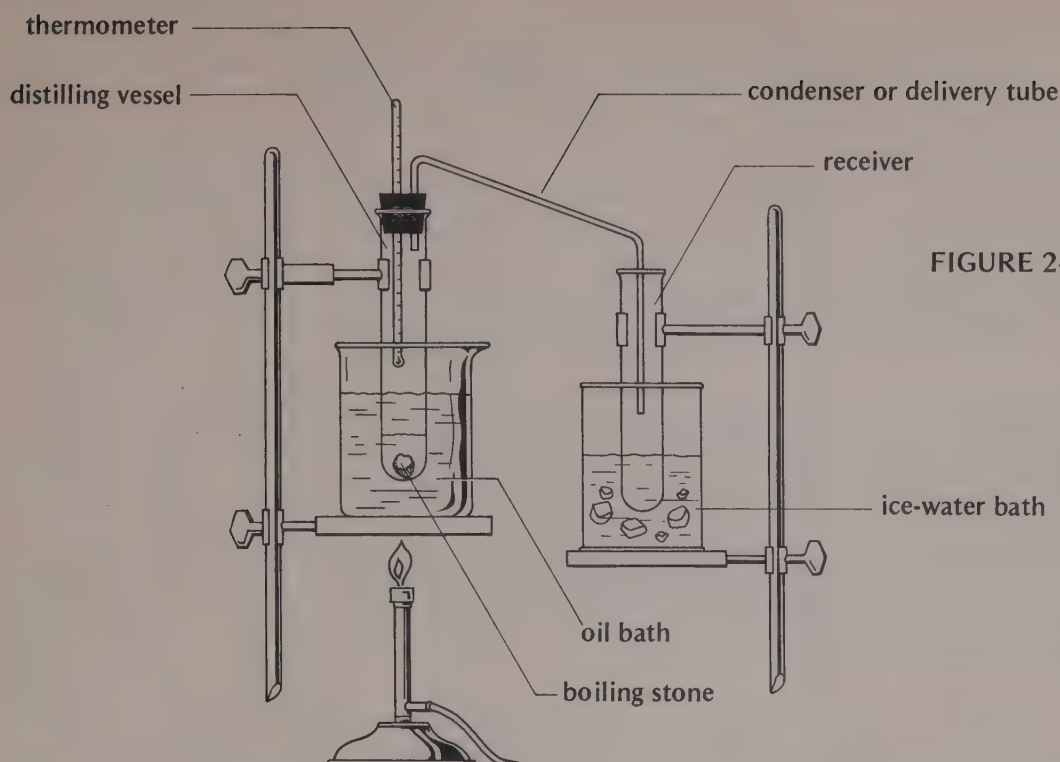


FIGURE 2-8: Distillation apparatus for Experiment 2-6.

ORGANIC EXPERIMENT 2-6 SIMPLE AND FRACTIONAL DISTILLATION

Purpose: To learn a technique for separating the components of a liquid mixture.

Materials

- | | |
|---|-------------------------------------|
| 2 ringstands with rings | 2 two-holed stoppers |
| 2 clamps | 35 ml methanol |
| 2 pieces asbestos gauze | 4 boiling stones |
| 2 tin cans, 8 oz, or 2 beakers, 200 ml | 1 thermometer, 0°C to 150°C |
| 6 test tubes, 25 mm x 200 mm | glass tubing (for condenser) |
| 25 ml water colored with a small amount of copper sulfate | 150 ml mineral oil or vegetable oil |
| 1 graduated cylinder, 50 ml | ice |
| | Bunsen burner |

PART I: DISTILLATION OF AN AQUEOUS SOLUTION

1. Assemble the apparatus shown in Figure 2-8.
2. Put 25 ml of the colored water in the test tube (the distilling vessel) immersed in the oil bath and add two boiling stones.
3. Make certain that the stopper is tight and that the condenser is not clogged. Immerse the receiver in an ice-water bath.
4. Heat the oil bath until the colored solution in the distilling flask begins to boil. Lower the flame on the Bunsen burner and continue to heat the oil just enough to keep the solution boiling and the vapor distilling.
5. Record the temperature of the vapor at 2-min intervals during the distillation.
6. Continue distilling until 4 to 5 ml of the solution remains in the distilling flask. **DO NOT DISTILL TO DRYNESS.**
7. What is the color of the distillate (the liquid in the receiver)? What is the color of the residue in the distilling flask? Explain.

PART II: DISTILLATION OF METHANOL

1. Clean and dry the condenser and the thermometer, and reassemble the distillation apparatus using clean, dry test tubes.
2. Place 20 ml of methanol and two boiling stones in the distilling flask and distill the methanol just as you distilled the water.

- Record the temperature of the vapor at several intervals during the distillation.
- Continue the distillation until about 5 ml of methanol remains in the distilling flask.

PART III: DISTILLATION OF A METHANOL-WATER MIXTURE

- Once again reassemble the apparatus using clean test tubes.
- Pour 15 ml of methanol and 15 ml of water into the distilling flask, and add two boiling stones.
- Begin distilling the mixture. Record the temperature when the first drops of distillate are collected. Record the temperature every 2 min after that.
- Change receivers when the temperature reaches about 85°C.
- Continue distilling until approximately 5 ml remains in the distilling flask.

Questions

- Compare the boiling point of water with the distilling temperature of the aqueous solution of copper sulfate. Is there a significant difference? Why or why not?
- Compare the distilling temperature of the solution with the boiling point of methanol. Is there a difference?
- From the temperatures you recorded when distilling the methanol-water mixture, do you think you got a fairly clean separation? How do you think you might improve the separation?

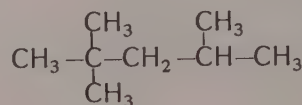
ORGANIC SECTION 2-7 OCTANE RATING AND CRACKING

The gasoline obtained directly from crude oil is called "straight run" (SR) gasoline. It cannot be used directly in automobiles because its octane rating is too low (around 70 to 75). This means that it burns too fast and causes engine knocking. Present day automobiles need gasoline with an octane rating of 88-93 (regular) to 94-100 (premium), although the most recent automobiles are designed to use low-lead or non-leaded gasoline with an octane rating of 87-92.

Octane rating is a measure of how smoothly a standard engine will run with a particular blend of gasoline. Higher octane gasolines give less knocking and more power. The octane rating is based on a comparison of a particular gasoline with a mixture of two compounds, heptane (with an octane rating of 0) and isooctane (with an octane rating of 100). A gasoline which knocks like a reference fuel containing 94 percent isooctane and 6 percent heptane has an octane rating of 94.



heptane

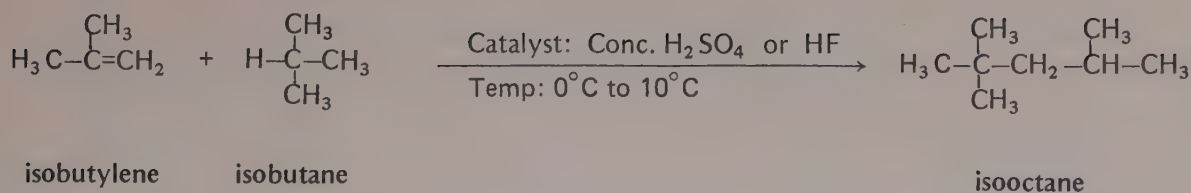


isooctane

The octane rating of SR gasoline is increased by adding branched-chain, unsaturated, and aromatic hydrocarbons, all of which have higher octane ratings than straight-chain hydrocarbons. Octane rating is also increased by the addition of other additives, the most common of which is tetraethyl lead. However, lead is now recognized as a dangerous pollutant, and efforts are being made to reduce its use in gasoline.

Catalytic and Thermal Cracking

In addition to the problem of increasing the octane rating of SR gasoline, companies have been attempting to find ways to produce more gasoline from each barrel of crude oil. When crude oil is distilled, about 20 percent of each barrel is obtained as gasoline. However, the demand for gasoline is so great that almost half of each barrel must be converted to gasoline. The oil companies have solved this problem by processes called *catalytic* and *thermal cracking*. In the cracking process, higher molecular mass hydrocarbons, the fuel oils, are broken into smaller hydrocarbons, which can be used as gasoline components. Oil companies also have devised processes for joining smaller hydrocarbons containing 2, 3 and 4 carbons to make larger molecules useable in gasoline. One such process involves the production of isooctane from isobutane and isobutylene.



With the reduction of domestic oil supplies and increasing price of imported oil, our society will be under continuing pressure to use less gasoline, as well as gasoline with lower octane ratings.

SUMMARY, PART TWO

Many terms can be used to classify hydrocarbons, including saturated, unsaturated, ring, and aromatic. Melting points and boiling points are physical properties which may indicate how the molecules of these compounds interact. Structural isomers can be produced by taking the atoms of one compound and rearranging them into a different structure. Although the molecular formulas of structural isomers are the same, the properties are different. Single bonds allow a free rotation of attached atoms; double and triple bonds lock the bonded atoms into a more rigid association. The double and triple bonds also make the compounds more reactive. Crude petroleum, one of the major sources of hydrocarbons, is separated into its components by the process of fractional distillation.

SUGGESTIONS FOR FURTHER STUDY

1. Draw structural formulas (or condensed formulas) for the straight-chain isomers of the first ten alkanes. Then investigate the branching possibilities. How many structures can you draw for C_5H_{12} and C_7H_{16} ?
2. The term "strain" is often used in relation to the compound cyclopropane. Could compounds with double and triple bonds be considered strained? If so, would the structural strain account for the reactivity of unsaturated compounds compared to saturated hydrocarbons?
3. Build a Styrofoam model of the benzene molecule.
4. Build a Styrofoam model of the cholesterol molecule.
5. Do some library research on the octane rating of automobile fuels. What kind of materials produce desirable ratings? Which materials produce undesirable ratings? Also find out which engines require high octane fuels and which do not. For example, what fuels do jet aircraft engines require?
6. Examine the structures of graphite and benzene and consider how they are alike.
7. Muscone and civetone are 15- and 17-membered ring compounds of carbon which are used in perfumes. Find out what you can about these interesting substances.

BIBLIOGRAPHY

Anon., "Be Sure You Understand Octane Numbers," *Chemistry*, January, 1974, p. 3.

Explains octane rating and additives of gasoline.

Anon., "Ethylene in Plants," *Chemistry*, March, 1975, p. 25.

Ethylene accelerates the ripening, sweetening, and rotting of plants. Propylene, butylene, and acetylene (all components of natural gas) have the same effect. Carbon dioxide counteracts the effects of ethylene; it is used to prevent spoilage in stored fruit. Plants produce their own ethylene naturally from an amino acid (methionine). In many respects ethylene acts as a plant growth hormone.

Ramsay, O. Bertrand, "Molecules in Three Dimensions," Part I, *Chemistry*, January, 1974, p. 6.

Models and various representations of organic molecules are discussed in a historical perspective.

PART THREE COMPOUNDS WITH FUNCTIONAL GROUPS

OBJECTIVES

When you have finished Part Three, you will be expected to demonstrate acceptable performance on the following learning objectives:

1. Write the structural formulas of four functional groups commonly found in organic compounds.
2. For each functional group that you have learned, write the structural formulas of two molecules containing that group.
3. Write an equation showing a typical reaction of each functional group.
4. Describe the uses of compounds containing the functional groups.
5. Write an equation which illustrates a substitution reaction.
6. Describe the changes in physical and chemical properties that occur when an alkyl group, attached to a particular functional group, is changed.
7. Write equations to illustrate the oxidation sequence from hydroxyl to carbonyl to carboxyl groups.
8. Write the structural formulas of two isomers whose molecular formula is C_2H_6O , and build models of each isomer.
9. Test a known carbonyl compound to determine whether it is an aldehyde or a ketone.
10. Write equations to show the formation of esters. Describe the properties of esters.
11. Write equations to show the formation of the aspirin molecule, and illustrate the parts of the molecule that determine its characteristic properties.
12. Describe the function of fats in living organisms.
13. Write the structural formulas of a soap and a detergent, circling the active portions of each molecule. Describe how they work.

ORGANIC SECTION 3-1 FUNCTIONAL GROUPS

Even though there are millions of organic compounds, they can be grouped into a small number of classes on the basis of their structures. For example, if a hydrogen atom is removed from an alkane molecule, the part of the molecule that remains is called an *alkyl group*.

Table 3-1: Some Simple Alkanes and Their Corresponding Alkyl Groups

Alkane	Molecular Formula	Alkyl Group
Methane	CH_4	methyl CH_3-
Ethane	CH_3CH_3	ethyl CH_3CH_2-
Propane	$CH_3CH_2CH_3$	propyl $CH_3CH_2CH_2-$
		isopropyl $\begin{array}{c} H_3C \\ \diagdown \\ CH- \\ \diagup \\ H_3C \end{array}$

Different groups of atoms known as *functional groups* can be attached to any of the alkyl groups. The chemical properties of the resulting compound are determined mainly by the functional group. To save space and time, the symbol R is often used in structural formulas to represent any alkyl group. Thus, the formula RH represents any alkane. The most important classes of organic compounds and their functional groups are shown in Table 3-2. (See page 25.) The symbols R' and R'' are used to represent a second and third alkyl group. The symbols R, R' and R'' may represent the same or different alkyl groups.

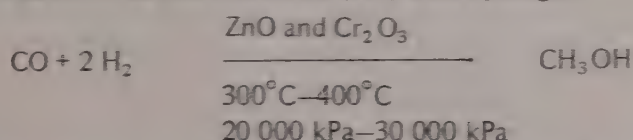
Table 3-2: Classes of Organic Compounds and Their Functional Groups

Class of Compound	Functional Group	General Formula	
Alkane	-H	RH	R-H
Alcohol	-OH	ROH	R-OH
Carboxylic Acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{-C} \\ \backslash \\ \text{OH} \end{array}$	RCOOH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R-C} \\ \backslash \\ \text{OH} \end{array}$
Aldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ \text{-C} \\ \backslash \\ \text{H} \end{array}$	RCHO	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R-C-H} \end{array}$
Ketone	$\begin{array}{c} \text{O} \\ \parallel \\ \text{-C} \\ \backslash \\ \text{R}' \end{array}$	RCOR'	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R-C-R}' \end{array}$
Ester	$\begin{array}{c} \text{O} \\ \parallel \\ \text{-C} \\ \backslash \\ \text{O-R}' \end{array}$	RCOOR'	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R-C-O-R}' \end{array}$
Ether	-O-R'	ROR'	R-O-R'
Amine	$\begin{array}{c} \text{H} \\ \\ \text{-N} \\ \\ \text{H} \end{array}$	RNH ₂	$\begin{array}{c} \text{H} \\ \\ \text{R-N} \\ \\ \text{H} \end{array}$

Compounds in the same class have the same functional group. They also display very similar chemical reactions, since chemical behavior is largely determined by the functional group. Therefore, we can usually predict how a compound will react on the basis of its functional group, even if we have not studied the compound before.

ORGANIC SECTION 3-2 ALCOHOLS: ROH

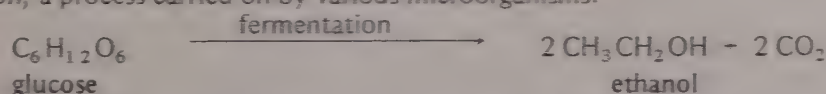
The functional group for alcohols is the hydroxyl (-OH) group. You have already encountered methanol, or methyl alcohol (page 10), and have seen that the -OH group is responsible for some of its properties. Methanol is often called wood alcohol, because its principal source was once the decomposition of hardwood bark. Today, the main commercial source of methanol is a catalyzed reaction of carbon monoxide (CO) with hydrogen:



During Prohibition (in effect from 1920 to 1933), when the use of alcoholic beverages was outlawed in the United States, many people tried to substitute methanol for ethanol. The unhappy result was that large numbers of people were blinded or fatally poisoned. The difference in effects of methanol and ethanol on the human body points up the fact that the functional group is not the only part of the molecule that matters.

Alcoholic Beverages

Ethyl alcohol (ethanol), is probably the most famous alcohol. It is formed from glucose by *fermentation*, a process carried on by various microorganisms:



Fermentation of grapes produces wine; fermentation of apples produces hard cider; fermentation of grain produces beer and ale. The alcohol content of wine and cider generally does not exceed about 14 percent because at that concentration the microorganisms that produce the alcohol die of alcohol poisoning. Because alcohol in high concentrations kills microbes, it is useful as an external antiseptic.

In order to produce an alcoholic beverage in which the concentration of alcohol exceeds 14 percent, the fermentation mixture must be distilled. Distillation of wine produces brandy; the distillation of beer and ale produces whiskey; and the distillation of fermented potatoes produces

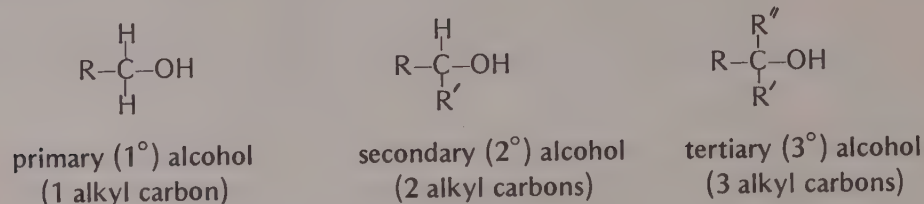
vodka. The distilled liquids are colorless and almost tasteless. It is only after they are stored in wooden barrels (a process called "curing") that they acquire color and flavor.

Proof: The Concentration of Alcohol in a Beverage

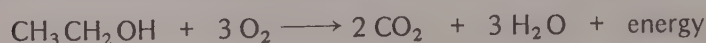
Proof is a measure of the alcoholic concentration in a liquor on a scale where a defined "proof spirit" is rated at 100. The term arose in the days when alcohol measurements could not be made accurately. Distillers used certain crude tests and looked for particular signs that the liquor had achieved the desired alcohol concentration—"proof" of the suitability of the beverage. The definition of 100-proof varies from country to country. In the U.S., it is 50% alcohol by volume; in Canada, it is 57.1%.

Reactions of Alcohols

To account for differences in the behavior of different alcohols, it is useful to classify alcohols according to the number of carbon atoms bonded directly to the alkyl carbon next to the hydroxyl group:

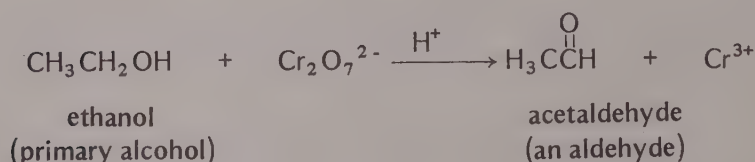
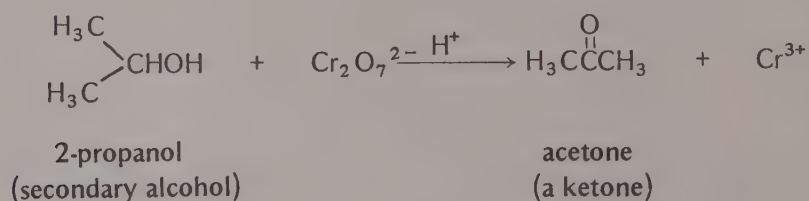


Alcohols readily undergo oxidation. The most extreme form of oxidation is combustion:



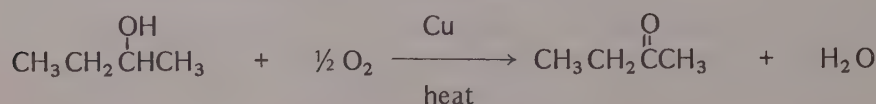
Combustion occurs in an alcohol lamp or a Sterno can. Some people are now suggesting that gasoline can be conserved by adding an alcohol (methanol) to it.

Milder oxidation of alcohols can be brought about by reacting them with oxidizing agents, such as potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and potassium permanganate (KMnO_4). Mild oxidation of primary alcohols produces aldehydes; secondary alcohols give ketones. Tertiary alcohols do not undergo this type of oxidation.

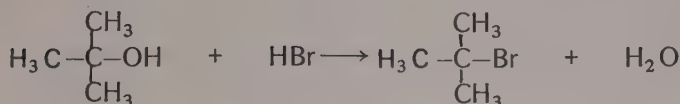
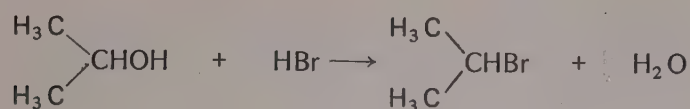
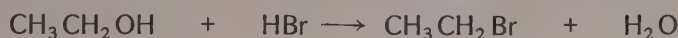


In organic chemistry *oxidation* always results either in adding oxygen or removing hydrogen (or both). Elemental oxygen is sometimes added, as in combustion. More often, however, oxygen is furnished by an oxidizing agent such as the dichromate ion. When a compound undergoes reduction, the reaction is the opposite of oxidation. In *reduction*, hydrogen is added or oxygen is lost (or both). Can you find an example of a reduction reaction earlier in this section?

The direct removal of hydrogen from alcohols can be accomplished by passing a heated mixture of air and alcohol vapor over a copper catalyst.



A typical chemical reaction which almost all alcohols undergo is *substitution* of the -OH group by a halogen (Cl , Br , I):



All three of the alcohols in these examples undergo essentially the same reaction; but if we compare their reactivities, we find that they do not all react at the same speed. Even though the alkyl groups do not seem to undergo any change, they nonetheless affect the reactivity of the functional group.

Chemists concentrate on functional groups of molecules in the same way that surgeons concentrate on the part of the patient not covered by the sheets. The uncovered part is where the action is. However, we can't ignore the rest of the molecule any more than a surgeon can ignore the rest of his patient. Otherwise he may end up having to cover the entire patient with a sheet. In Experiment 3-1 you will investigate the relationships between the structure of alcohols and their reactivities.

ORGANIC EXPERIMENT 3-1 SOME REACTIONS OF ALCOHOLS

This experiment is similar to Experiment 2-1. Its focus is on the behavior of the -OH functional group. You will test seven alcohols, first for reactivity with an oxidizing agent, and then for reaction with concentrated hydrochloric acid. The test alcohols are listed in Table 3-3. Some of the reactions may be rather slow, so allow them to continue for the duration of the laboratory period. Observe each reaction tube periodically, and record the amount of time that elapses before a change (if any) occurs in each tube.

Table 3-3: A Group of Alcohols and Their Formulas

methanol	CH_3OH	1-butanol (butyl alcohol)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	2-butanol (<i>sec</i> -butyl alcohol)	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3\text{CH}_2\text{CHCH}_3 \end{array}$
1-propanol (propyl alcohol)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	2-methyl-2-propanol (<i>tert</i> -butyl alcohol)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$
2-propanol (isopropyl alcohol)	$\begin{array}{c} \text{OH} \\ \\ \text{H}_3\text{CCHCH}_3 \end{array}$		

Purpose: To investigate the relationship between the structure of alcohols and their properties.

Materials

10 ml of each of the alcohols listed in
Table 3-3
35 ml 12 M HCl
40 ml 0.015 M $\text{K}_2\text{Cr}_2\text{O}_7$ in 3 M H_2SO_4
8 test tubes, 13 mm x 100 mm
8 stoppers to fit test tubes

Bunsen burner
1 test tube, 18 mm x 150 mm
1 test tube rack
safety goggles

Procedure

PART I: THE REACTIONS OF ALCOHOLS WITH MILD OXIDIZING AGENTS

1. Prepare a data table in which to record the starting and ending times for each reaction performed in this part. Now look up the boiling points of each of the seven alcohols in a handbook, and record these in your data table.
2. As a reference reaction, mix 1 ml of ethanol with 5 ml of the oxidizing solution (0.015 M $\text{K}_2\text{Cr}_2\text{O}_7$ in 3 M H_2SO_4). Stopper the tube and shake it once or twice to mix its contents. Observe the tube for a few minutes. (If you hold a white piece of paper behind the test tube, the color change may be easier to see.)
3. Mix 1 ml of each of the other alcohols with 5 ml of the oxidizing solution. Record the starting and ending time for each reaction. Any color changes that occur may be more visible if you hold a piece of white paper behind the reaction tubes.

PART II: THE REACTIONS OF ALCOHOLS WITH HCl

Carefully add 5 ml of 12 M HCl to 1 ml of each of the alcohols. Stopper each tube and shake for at least 1 minute. The appearance of cloudiness in the solution is evidence of a reaction. The product may remain in solution or it may settle out. Record your observations.

Questions

1. Examine the structural formulas of all the alcohols you have studied. Which compounds are isomers of each other? Which compounds are the most similar in structure?
2. As the alcohol molecules increase in size, how do their boiling points change? Compare the boiling points of the structural isomers. What relationships do you find?
3. What relationships exist between the structures of the alcohols and their reactivities with the oxidizing agent $\text{K}_2\text{Cr}_2\text{O}_7$?
4. The reaction between an alcohol and concentrated hydrochloric acid produces an *alkyl chloride*, R-Cl. Write an equation for this reaction. Be sure to include all the products.
5. How do the reactivities of the alcohols with concentrated HCl compare?
6. In addition to the forms of butyl alcohol used in this experiment, there is a fourth alcohol with the formula $\text{C}_4\text{H}_9\text{OH}$. Draw its structural formula. Where do you think this isomer would fit into your ranking of reactivities with concentrated HCl? (See Question 5.) Explain.

ORGANIC SECTION 3-3 ETHERS: ROR'

Alcohols are derived from water by replacing one of the hydrogen atoms with an alkyl group. Ethers are the dialkyl derivatives of water—that is, both of water's hydrogen atoms are replaced by alkyl groups. (R and R' may represent the same alkyl group, or different groups.)



water



alcohol



ether

As you might predict from their structural similarity, alcohols and ethers have many properties in common. Diethyl ether, $\text{CH}_3\text{CH}_2\text{—O—CH}_2\text{CH}_3$, is the most important ether. It is used as an anaesthetic and as a chemical solvent.

ORGANIC EXPERIMENT 3-2 MODEL BUILDING: ETHANOL AND DIMETHYL ETHER

Purpose: To construct models of the two isomers of $\text{C}_2\text{H}_6\text{O}$ —ethanol and dimethyl ether.

Materials

2 black Styrofoam spheres
6 white Styrofoam spheres

1 red Styrofoam sphere
toothpicks

Background: Bond Angle Around Oxygen when Oxygen Bonds with Two Atoms

From earlier experiences in model building (Experiments 1-3, 2-2, 2-4) you know how large to make the H—C—H angles in both isomers of $\text{C}_2\text{H}_6\text{O}$. However, to construct your models,

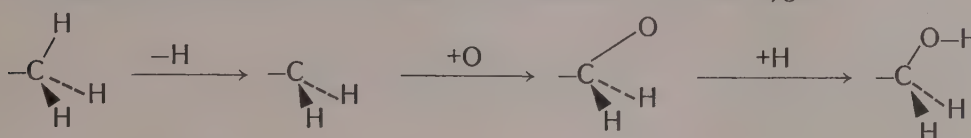
you must make a decision about how large to make the bond angles around the oxygen atom. In the drawing of the water molecule on page 73 of *Keys to Chemistry*, the H—O—H bond angle is shown to be 104.45° . We can use this figure as a guideline for the size of the angle around oxygen whenever it bonds with two other atoms.

You might wonder why the bond angle around oxygen is not 180° . The reason is that the two pairs of non-bonding electrons in oxygen take up space and repel one another, as well as repelling the electron pairs in the bonds holding the hydrogens. Water has a tetrahedral shape much like that of methane, with the non-bonding pairs of electrons taking the place of the two hydrogens.

With this bit of background on the bonding angle for oxygen and hydrogen, you can construct models of ethanol and dimethyl ether, using a model of ethane as a starting structure.

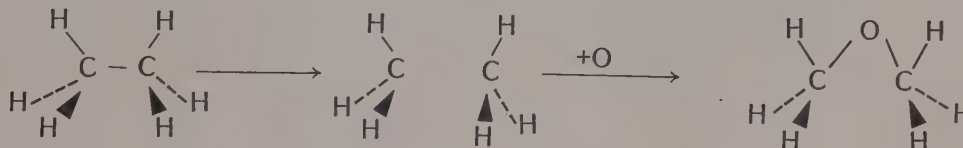
Procedure

1. Build a model of ethane, as you did earlier in Experiment 2-2.
2. Modify the ethane model to make ethanol. Remove one of the hydrogen spheres from your ethane model, and replace it with an oxygen atom (red Styrofoam sphere). Then take the hydrogen you removed from the carbon and connect it to the oxygen:



The C—O—H bond angle should be about 105° (almost a tetrahedral angle). Compare this model of ethanol with the “space-filling” diagram of ethanol on page 264 of *Keys to Chemistry*.

3. By modifying your ethane model slightly, you can construct a model of dimethyl ether. Separate the two carbon atoms in ethane. You now have two identical CH_3 units (methyl groups). Attach the two CH_3 groups to a single oxygen sphere. Use 105° as the C—O—C bond angle.



Questions

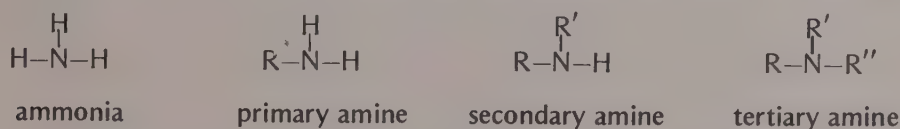
1. Compare the models of ethanol and dimethyl ether. On the basis of your models, can you account for the differences in physical properties?
2. Which compound do you expect to be more like water in its chemical properties?

Suggestions for Further Study

The actual C—O—C bond angle in dimethyl ether is 111.7° . What causes the bond angle around oxygen to be so much greater in dimethyl ether than it is in water? Build a model of water and compare it to the dimethyl ether model.

ORGANIC SECTION 3-4 AMINES: RNH_2

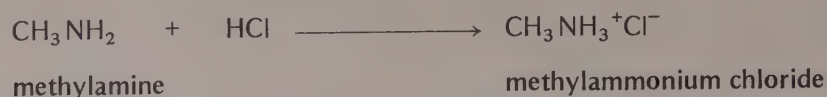
Amines are related to ammonia in the same way that alcohols and ethers are related to water:



Ammonia and amine molecules have tetrahedral shapes, just as water and methane do. (See page 8.) In ammonia one pair of electrons and three hydrogen atoms occupy the corners of the tetrahedron. Each H—N—H bond angle is 107° . (See *Keys to Chemistry*, page 178.)

If you have made the prediction that amines resemble ammonia in their chemical behavior, you are right. For example, as a base methylamine has about the same strength as ammonia.

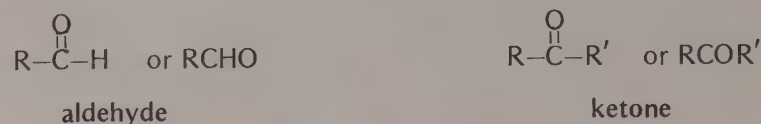
Methylamine reacts with strong acids such as hydrogen chloride as follows:



In what way is the reaction of methylamine with HCl similar to the reaction of NH_3 with HCl?

ORGANIC SECTION 3-5 ALDEHYDES AND KETONES: RCHO AND RCOR'

In Section 3–2, you learned that aldehydes and ketones are the products of the mild oxidation of primary and secondary alcohols. The functional group of both aldehydes and ketones is the carbonyl group ($>\text{C}=\text{O}$), distinguished by the presence of a carbon–oxygen double bond. In aldehydes the carbonyl group is bonded to one hydrogen atom and one alkyl group; in ketones it is bonded to two alkyl groups.

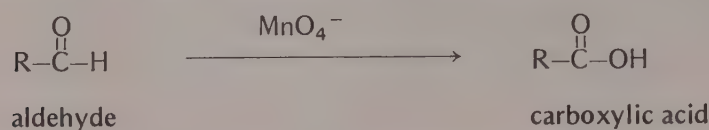


Reactions of Aldehydes and Ketones

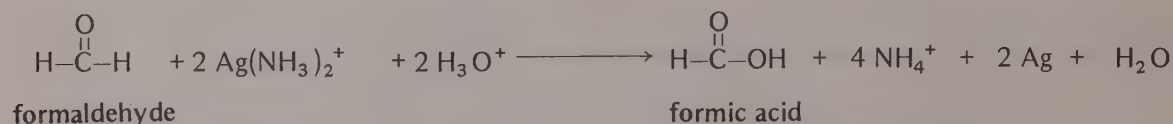
Aldehydes and ketones can be reduced back to the alcohols from which they are produced:



The biggest difference between aldehydes and ketones is that aldehydes, unlike ketones, can be further oxidized. In fact, aldehydes are so easily oxidized that special precautions must be used if an aldehyde is to be isolated as the product of oxidation of an alcohol. If such precautions are not taken, the aldehyde will be oxidized further to a carboxylic acid.



One of the most interesting ways to oxidize an aldehyde is with silver ion (which must be complexed with ammonia). The silver ion is reduced to metallic silver, which can be deposited on the bottom and sides of a test tube as a shiny mirror:



This formaldehyde reaction is useful as a test to distinguish aldehydes from ketones. The reaction also can be used for (you guessed it) making mirrors.

ORGANIC EXPERIMENT 3-3 A TEST TO DISTINGUISH ALDEHYDES FROM KETONES

Purpose: To test a method for distinguishing aldehydes from ketones.

Materials

- | | |
|---------------------------------------|--|
| 1 test tube, 18 mm x 150 mm | 1 beaker, 250 ml |
| 1 stopper to fit test tube | warm water |
| 1 test tube rack | dropper bottles containing various test compounds, such as formaldehyde, benzaldehyde, and acetone |
| 10 ml 0.01 M AgNO_3 solution | |
| 5 ml 0.1 M NaOH solution | |
| 25 ml 0.1 M ammonia solution | |

Procedure

In a scrupulously clean test tube place 2 ml of 0.01 M silver nitrate solution, and add a drop of 0.1 M sodium hydroxide. Add 0.1 M ammonia drop by drop, with constant shaking, until the precipitate of silver oxide just dissolves. Add a drop of the test compound. If no reaction takes place at room temperature, warm the test tube in a beaker of warm water for no more than 5 minutes. CAUTION: Whether or not a positive test is obtained, the mixture should be flushed down the drain within a few minutes, since a dangerous precipitate tends to form on standing.

Apply this test to formaldehyde, benzaldehyde, and acetone (or to any other compounds suggested by your instructor).

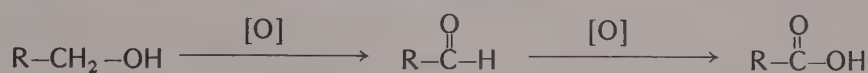
Questions

1. What is formed in a positive test?
2. What compound would benzaldehyde form?
3. What compound would acetaldehyde form?

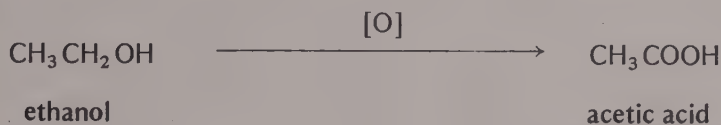
ORGANIC SECTION 3-6 CARBOXYLIC ACIDS: RCOOH

The functional group of the carboxylic acids, the carboxyl group ($-\text{COOH}$) is the combination of two functional groups: a carbonyl group (*carb-*) attached to a hydroxyl group (*-oxyl*). However, in this case the whole is greater than the sum of its parts: carboxylic acids have some of the characteristics of alcohols, and some of the characteristics of aldehydes and ketones. And, in addition, they have unique properties of their own.

In Section 3-5, you learned that carboxylic acids result from the oxidation of aldehydes, and that aldehydes can be obtained from the oxidation of primary alcohols. It shouldn't come as a surprise, therefore, to discover that primary alcohols can be converted directly to carboxylic acids without first isolating the intermediate aldehyde.



For example, when wine sours, the ethanol in the wine is oxidized to acetic acid, producing wine vinegar:

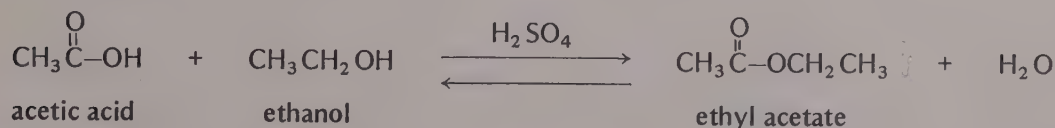


What do you think the oxidizing agent is in this reaction?

The most important chemical property of carboxylic acids is their acidity. (See *Keys to Chemistry*, Chapter 4.) Compared with the common mineral acids such as sulfuric, nitric, and hydrochloric acid, the carboxylic acids are weak.

ORGANIC SECTION 3-7 ESTERS: RCOOR'

When an organic acid reacts with an alcohol, an ester results:



Esters are named after their parent alcohols and acids. For example, the ester propyl formate is made from propyl alcohol and formic acid. Try writing the equation for the formation of this ester.

Esters have pleasant odors, and many of them are found in plants and fruits. Insects use esters to send chemical messages to each other. For example, to attract a mate, a female fly produces a small amount of an extremely potent sex attractant. The ability of sex attractants to "call in"

all the males (or female) insects of a species to a small area can serve as a very effective means of insect control. Once they are in the small area, the insects can be trapped or killed by insecticides. As a result, insects can be controlled without destroying other forms of life. The sex attractants of the gypsy moth and the cotton-boll weevil have been isolated and chemically synthesized. The synthetic attractants are being used to control these crop damaging insects.

ORGANIC EXPERIMENT 3-4 PREPARATION OF A TYPICAL ESTER

Purpose: To illustrate the typical procedure used to prepare esters.

Materials

1 ringstand and ring	1 test tube holder
wire gauze	1 beaker, 400 ml
1 test-tube clamp	1 stirring rod
1 Bunsen burner	2 ml glacial acetic acid
safety goggles	2 ml pentyl alcohol
1 test tube, 25 mm x 200 mm	1 ml concentrated sulfuric acid

CAUTION: Wear safety goggles as you do this experiment.

Procedure

1. Cautiously waft vapors from the acetic acid bottle and the pentyl alcohol bottle toward your nose. Note the odor of each and record a description of the odors.
2. Use a test tube as a reaction vessel. First, place 2 ml of the glacial acetic acid in the tube. Then add 2 ml of pentyl alcohol and 5 drops of concentrated sulfuric acid. Add the sulfuric acid very carefully, stirring gently to mix the reactants.
3. Suspend the reaction vessel in a boiling water bath. After several minutes, waft vapors from the reaction toward your nose. Does a new odor exist which would indicate a product different from the two reactants? If so, describe the odor.
4. Dispose of the materials as directed by your teacher.

Questions

1. Write the equation for the reaction.
2. Is there any evidence that would suggest the existence of an equilibrium in this reaction?
3. Why is sulfuric acid used? How might sulfuric acid shift an equilibrium state toward the products?
4. Suggest a name for the ester prepared in this experiment.

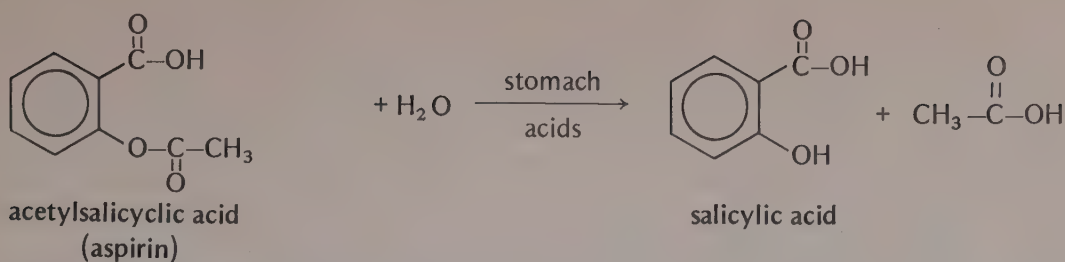
Suggestions for Further Study

1. What would you need to do to isolate a pure sample of the ester prepared in this experiment?
2. How would you establish that you actually prepared an ester?

ORGANIC SECTION 3-8 ASPIRIN: A VERY FAMOUS DRUG

One of the most useful drugs we know is aspirin, an organic compound that is both an acid and an ester. In fact, aspirin is the most widely used drug in the world. Ancient people discovered that if they chewed the bark of the willow tree, their aches and pains were relieved and their fevers were reduced. Chemists subsequently discovered that the active ingredient in willow bark is salicylic acid. However, salicylic acid is extremely sour. So chemists attempted to remove the undesirable properties of the molecule without eliminating its beneficial effects.

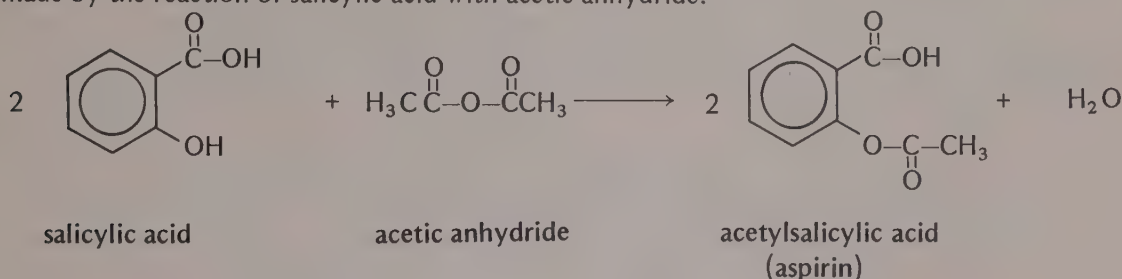
In 1889 acetylsalicylic acid was introduced. Today's aspirin tablets usually contain 5 grains (1 grain=0.065 g) of acetylsalicylic acid held together with a binder such as clay, starch, or sugar. Acetylsalicylic acid is converted to salicylic acid in the stomach.



Since aspirin is an acid, some people experience stomach irritation if they take it on an empty stomach. For this reason, some people prefer to use buffered aspirin, which contains antacids along with the active ingredient, acetylsalicylic acid.

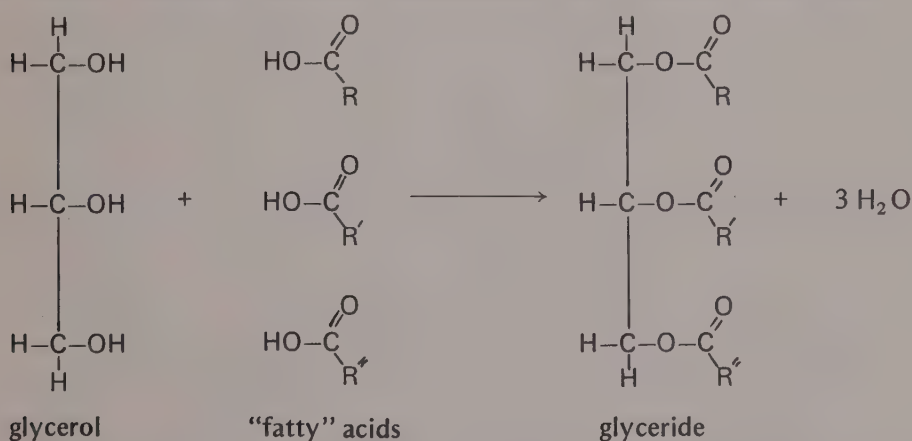
Synthesis of Aspirin

Salicylic acid has two functional groups—a carboxyl group and a hydroxyl group. Compounds having a hydroxyl group attached directly to an aromatic ring are known as *phenols*. Phenols are the aromatic counterparts of alcohols. To convert salicylic acid into aspirin, an ester, the hydroxyl group must be converted to an ester group while leaving the carboxyl group unchanged. Phenols are most easily converted into esters by treating them with a carboxylic anhydride—a derivative of the acid which is more reactive than the free acid. Consequently, aspirin is made by the reaction of salicylic acid with acetic anhydride.



ORGANIC SECTION 3-9 FATS AND OILS: A SLIPPERY BUSINESS

Corn oil, coconut oil, cottonseed oil, olive oil, margarine, butter, bacon grease, and lard are all examples of fats and oils of vegetable and animal origin. Fats are a special kind of ester, formed from the trihydric alcohol, glycerol, and long-chain carboxylic acids, known as “fatty” acids. Most fats are mixtures of the glycerol esters (glycerides) of several “fatty” acids.



Fatty acids are carboxylic acids that have an even number of carbon atoms; the common ones range from 12 to 20 carbon atoms. Some fatty acids have carbon-carbon double bonds (unsaturated acids) and others do not (saturated acids). Liquid oils contain high percentages of unsaturated glycerides; in the solid fats, saturated glycerides predominate.

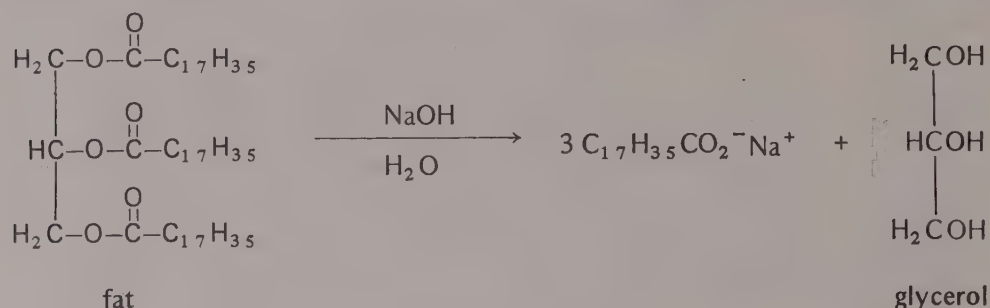
Importance of Fats in Nutrition

Fats are important to humans and animals because they act as energy storage molecules. Body fat comes not only from fats that are eaten directly, but also from fats that are produced from

carbohydrates. When extra energy is needed, the fats are first broken into simpler soluble molecules. Eventually they are converted to carbon dioxide and water.

ORGANIC SECTION 3-10 SOAPS AND DETERGENTS

You know from experience that soaps and detergents can cut grease. In order for a soap to clean, it must be able to dissolve the greasy dirt (hydrocarbons) in water. Soaps, therefore, must be soluble in both non-polar and polar substances. Salts of fatty acids, such as sodium stearate, $C_{17}H_{35}CO_2^-Na^+$, meet both requirements. To make soap, a fat is boiled with sodium hydroxide:



The resulting soap is a mixture of sodium stearate, as shown above, and the sodium salts of other fatty acids. The exact composition depends on the source of the fat or oil.

How does soap work?

What makes soap a good cleaning agent? Soap's ability to clean is a result of its ability to dissolve in both fats and water. One end of the molecule (the hydrocarbon end) is fat soluble; the ionic end ($-\text{CO}_2^-Na^+$ or $-\text{CO}_2^-K^+$) is water soluble.

One aspect of soaps that makes them less than perfect as cleaning agents is that they react with calcium ions and magnesium ions. The resulting compounds are not very soluble in water. In fact, they form a precipitate—a scum which gets into clothes and forms rings in the bathtub. Calcium and magnesium ions are quite commonly found in “hard water”.

There are two ways to eliminate the “bathtub ring” effects of soap in hard water. One solution is to remove the ions from the water. Water softeners do just that; they tie up the calcium and magnesium ions so that they are either removed from the water or held in soluble compounds. The second solution is to invent compounds which act as cleaning agents without also reacting with calcium and magnesium ions to form a precipitate. Invention of such compounds became possible once chemists were able to understand how soaps work. They began searching for other molecules which have a long hydrocarbon tail and an ionic group at one end. They found that salts of long-chain sulfonic acids (known as sulfonates) had the ability to act as cleaning agents. Sulfonates have the formula $R-\text{SO}_3^-Na^+$. The common name for these compounds is detergents.

Soaps are made from animal fats. Synthetic detergents, however, are usually derived from petroleum products. In contrast to soaps, whose cleaning power can be blocked by hard water, detergents act in hard or soft water. To enhance the action of detergents, polyphosphate ions are added. They combine with calcium and magnesium ions, forming soluble compounds. Unfortunately, phosphates also act as nutrients for algae growth. As a result, detergent phosphates that drain into lakes and rivers can promote algal blooms. These blooms deplete the oxygen supply of the water, leading to the death of fish.

Another problem with detergents is that many of them cannot be acted upon by biological organisms. This means they cannot become a part of a natural chemical cycle. Once they are introduced into the water supply, they continue to exist. In fact, you have probably seen white detergent foams on rivers and lakes.

SUMMARY, PART THREE

Part Three has focused on the chemical properties of the functional groups of organic compounds. By now, you are beginning to realize that each functional group is characterized by particular chemical reactions. In Part Four, the focus shifts to a consideration of physical properties. As

you develop an overall feeling for the nature of organic chemistry, try to think about chemical and physical properties together.

SUGGESTIONS FOR FURTHER STUDY

1. Find a recipe for soap making in a laboratory manual or in a book on practical arts, and make your own soap.
2. Find directions in a laboratory manual for preparing aspirin and try making some.
3. Wine making and beer making are major industries centered around the compound ethyl alcohol. Find out what you can about the production of these beverages.
4. Find out how acetic acid is made on a commercial scale.
5. In methane the tetrahedral angle is 109.46° . The H—O—H bond angle in water is 104.45° . The C—O—C bond angle in dimethyl ether is 111.7° . Try to explain why the bond angle in water is less than the tetrahedral angle, and why the bond angle in dimethyl ether is more than the tetrahedral angle.
6. The esters involved in the mating behavior of insects are called *pheromones*. See what you can find out about these compounds.
7. Oil spills seem to have become more prevalent during the last several years. Try to find out how oil spills have been cleaned up. Also consider and test some of your own ideas for cleaning up oil spills.
8. Do research on the properties of formaldehyde, acetaldehyde, and acetone, and find out how they are used. Also find out what precautions should be taken when these substances are used.

BIBLIOGRAPHY

Anon., "Rescuing Oil-Soaked Birds," *Chemistry*, June, 1973, p. 4.

Birds soaked by spilled oil can be washed in detergent and rinsed thoroughly. After the spilled oil has been removed, the birds begin to produce new skin and feather oils. After three weeks of rehabilitation they can return to their natural environment.

Labianca, Dominick A., "Methanol Poisoning—Biochemical Considerations," *Chemistry*, July–August, 1975, p. 19.

Methanol poisoning resulting from drinking or from prolonged skin contact may cause blindness and death. This article explores the chemical mechanism of methanol poisoning.

Ethyl alcohol, which competes with methanol metabolism, can counteract methanol poisoning.

Schneider, Dietrich, "Sex-Attractant Receptor of Moths," *Scientific American*, July, 1974, p. 28.

Moths communicate with certain esters called pheromones. The sex attractant of the female silk moth is detected by receptors on the antennae of the male. Just one molecule of attractant triggers a nerve impulse in the receptor cells. Includes excellent photographs and drawings of the receptor cells.

PART FOUR PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS

OBJECTIVES

When you have finished Part Four, you will be expected to demonstrate acceptable performance on the following learning objectives:

1. Explain how van der Waals forces are affected by molecular size and shape.
2. Explain how the degree of polarity of molecules affects the boiling point of the compound.
3. Describe hydrogen bonding and state how it affects boiling points.
4. Describe the relationship between the shapes of molecules and their melting points.
5. Describe the relationship between the chemistry of molecules and their solubility in water and other solvents.
6. Explain the solubility of a complex molecule like sucrose in water.
7. Explain why melting points and boiling points can be used as indicators of the strength of forces acting between molecules.

ORGANIC SECTION 4-1 INTERMOLECULAR FORCES OF ATTRACTION

Physical properties, such as boiling point, melting point, and solubility, depend on forces between molecules. These are called intermolecular forces. In the sections that follow you will see how intermolecular forces result from the size, shape, polarity, and hydrogen bonding properties of molecules.

Electrical Forces and Change of State

In order to melt a solid, the attractive forces holding the molecules in fixed positions in the crystal lattice must be overcome. The molecules must acquire enough energy so the forces can no longer hold them in position in the crystal. When the crystalline structure is broken, the molecules are free to move about, and the substance becomes liquid. If the molecules move still more energetically, and the forces between them are even less effective, the substance becomes a gas.

Individual molecules can acquire enough energy to vaporize at almost any temperature. However, to vaporize large numbers of molecules from a sample that is a liquid or solid at room temperature, heat must be added deliberately. The temperature of the sample is usually raised to the boiling point. The boiling point is reached when the pressure of the escaping molecules equals the pressure of the atmosphere over the liquid.

Molecules with strong attractive forces tend to exist as solids. They also tend to have high melting points. Conversely, those with weak attractive forces tend to exist as gases; they have lower boiling points and melting points than strongly polar compounds.

Polar and Non-Polar Organic Compounds

The forces of attraction between different compounds may affect how they behave. For example, if a solid is to dissolve in a solvent, the forces of attraction holding the molecules together in the solid must be overcome. The solid dissolves in a solvent if the attractive forces between the solute and the solvent are stronger than the forces holding the solid together. (For a review of the nature of these intermolecular forces, see Sections 7-3 and 7-5 of *Keys to Chemistry*.)

You can predict some of the properties of organic compounds by determining which molecules are polar and which are non-polar, and by examining the degree of polarity. Hydrocarbons are non-polar or only slightly polar. The reason for this is the small difference in the electronegativities of carbon and hydrogen, and in the charge symmetry (balanced arrangement) of the atoms in the molecules. (Review pages 182 and 190-192 in *Keys to Chemistry*.) Ethers and alkyl halides are slightly polar because of the difference in the electronegativities of carbon and oxygen, or carbon and halogen, and also because of the shape of the molecules. In these non-polar or weakly polar compounds—hydrocarbons, alkyl halides, and ethers—the van der Waals forces are the most important forces of attraction among the molecules.

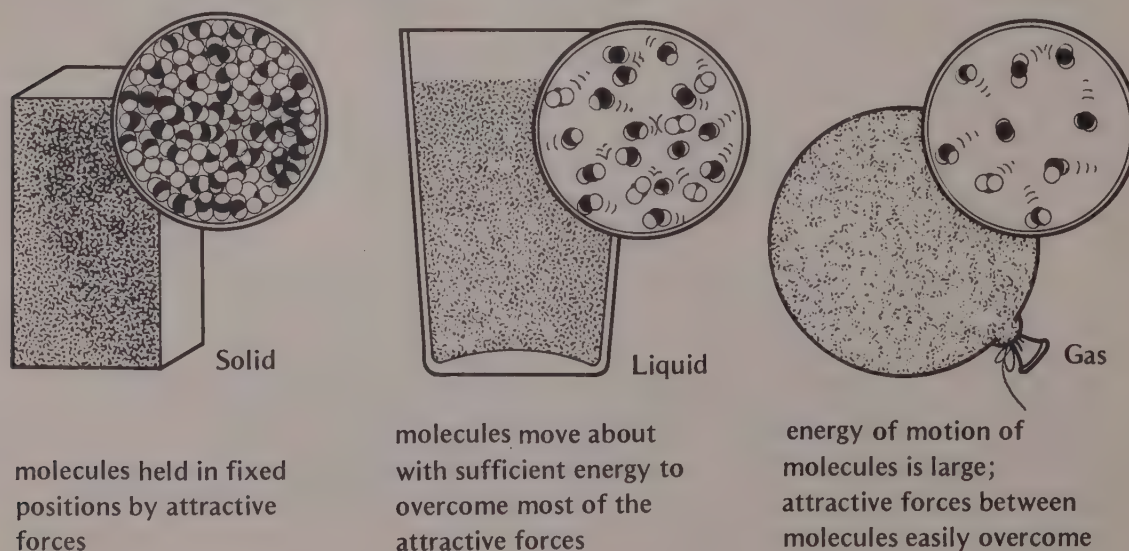


FIGURE 4-1: Molecular characteristics of solids, liquids, and gases.

ORGANIC SECTION 4-2 HEAVIER COMPOUNDS HAVE HIGHER BOILING POINTS

You will recall that the strength of the van der Waals forces depends on the size of the molecules and hence, on their molecular masses. Look at the table you constructed for Experiment 2-3. Notice that the boiling points increase as the molecular masses of alkanes increase. If you continued the table to include hydrocarbons of higher molecular mass, you would find that the boiling points continue to increase as the molecular masses increase.

The molecular masses and boiling points for several alkanes, alkyl halides, and ethers are listed in Table 4-1. Two things, in particular, stand out in this table. The first is that the boiling points increase regularly with increasing molecular mass. The second is that the boiling points are about the same for alkanes, ethers, and alkyl halides having the same molecular mass.

In summary, the boiling points for compounds which are non-polar or only slightly polar depend almost entirely on the strength of the van der Waals attractions among the molecules. The strength of the van der Waals forces changes with molecular masses.

Table 4-1: Boiling Points of Alkanes, Ethers, and Alkyl Chlorides

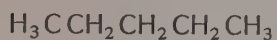
	Molecular Mass	Boiling Point °C		Molecular Mass	Boiling Point °C
propane	44	-42	hexane	86	69
dimethyl ether	46	-24	butyl methyl ether	88	70
methyl chloride	50	-24	butyl chloride	92	79
butane	58	0	heptane	100	98
ethyl methyl ether	60	10	dipropyl ether	102	90
ethyl chloride	64	13	pentyl chloride	106	108
pentane	72	36			
diethyl ether	74	35			
propyl chloride	78	47			

ORGANIC SECTION 4-3 MOLECULAR SURFACE AREAS AND SHAPES AFFECT BOILING POINTS

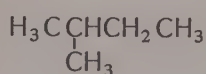
The strength of van der Waals forces depends on the *surface areas* of molecules. The surface areas, in turn, depend on the sizes of the molecules—thus the connection with molecular mass.

The surface areas also depend on the *shapes* of the molecules. The dependence on molecular shapes shows up when the molecular masses are very close together or identical, as in the case of isomers. Consequently, the compounds of the same molecular mass have different boiling points if the molecules are shaped differently.

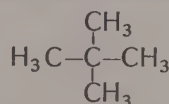
In Section 2-3, you worked out structural formulas for three isomeric alkanes having the molecular formula C_5H_{12} . These isomers are shown below, along with their boiling points.



pentane
b.p. 36°C



isopentane
b.p. 28°C



neopentane
b.p. 10°C

The pentane molecules have the largest surface areas, hence the strongest van der Waals attractions and the highest boiling point. The neopentane molecules are the most compact; they have the smallest surface areas and the lowest boiling point.

The general rule among isomers is that the more highly branched compounds have the lowest boiling points. The straight chain isomers always have the highest boiling point. Straight chains have the greatest surface areas, and thus more opportunity for contact between molecules.

ORGANIC SECTION 4-4 POLARITY RAISES BOILING POINTS

A bond between atoms of different electronegativities is a *polar bond*. Bond polarity results from unequal sharing of electrons. Unequal electron sharing causes a slight negative charge on the more electronegative atom of a bonded pair, and a slightly positive charge on the other atom. Molecules containing polar bonds are usually polar molecules. (Exceptions arise when polar bonds are symmetrically arranged, thus neutralizing polarity. Carbon tetrachloride is an example.) The greater the polarity within a molecule, the stronger are the attractions between molecules. This increased polarity is reflected in higher boiling points.

The boiling points and molecular masses of several aldehydes and ketones are shown in Table 4-2. Compare these boiling points with those given in Table 4-1 for less polar compounds. Notice that the boiling points are generally higher for aldehydes and ketones than for alkanes, ethers, or alkyl halides of comparable molecular mass. Can this be explained on the basis of their structure?

Table 4-2: Boiling Points of Aldehydes and Ketones

	Molecular Mass	Boiling Point °C		Molecular Mass	Boiling Point °C
acetaldehyde	44	21	valeraldehyde	86	103
propionaldehyde	58	50	methyl propyl ketone	86	102
acetone	58	56	caproaldehyde	100	128
butyraldehyde	72	74	butyl methyl ketone	100	129
ethyl methyl ketone	72	80			

Molecules containing different elements joined by double or triple bonds are much more polar than molecules in which different atoms are joined by single bonds. For example, compounds containing carbonyl groups (carbon-oxygen double bonds) are more polar than ethers, in which oxygen is joined to two carbons by single bonds.

Dipole-Dipole Attraction

Why are intermolecular attractions stronger in polar molecules than in non-polar molecules? You are already aware that ions of opposite charge attract each other. Similarly, the positive end of a polar molecule will be attracted to the negative end of a nearby molecule. This mutual attraction is known as *dipole-dipole attraction*. A *dipole* is a molecule with a positively charged end and a negatively charged end. The dipole-dipole attractions, along with the ever-present van der Waals attractions, cause the attractive forces in polar substances that result in higher boiling points.

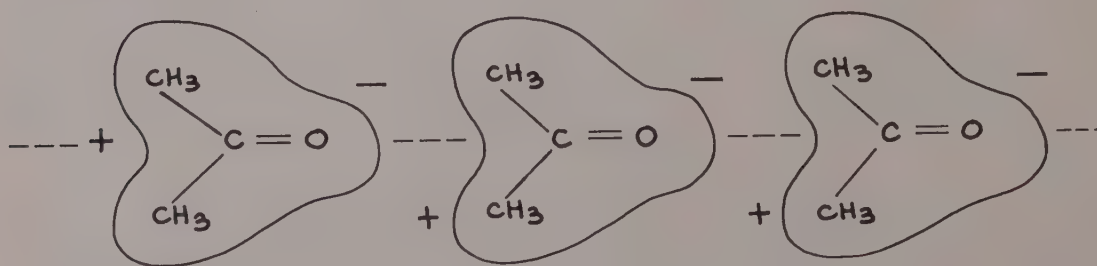


FIGURE 4-2: Dipole-dipole attractions between acetone molecules.

ORGANIC SECTION 4-5 HYDROGEN BONDS RAISE BOILING POINTS

You may remember that water molecules attract one another because of their tendency to form *hydrogen bonds*. Hydrogen bonds are the result of strong electrostatic attractions between the hydrogen of one molecule and the oxygen of another. (See *Keys to Chemistry*, pages 73 and 195.) You shouldn't be surprised, therefore, to learn that alcohol molecules are attracted to one

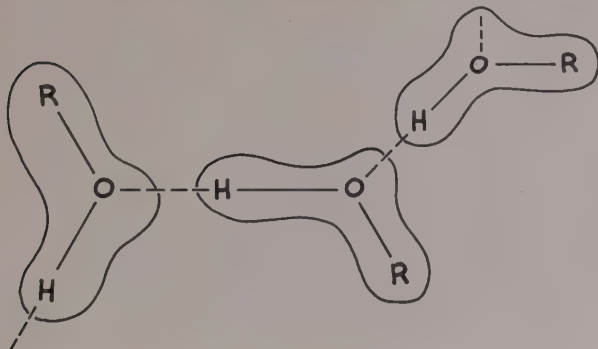
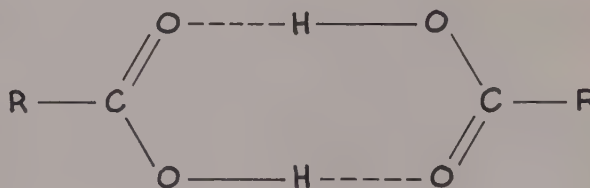


FIGURE 4-3: Hydrogen bonding between alcohol molecules. The dotted lines represent hydrogen bonds.

another in the same way. The strength of this attraction is greater than the strength of the dipole-dipole attractions of the compounds described earlier. As a result, alcohols have even higher boiling points than aldehydes and ketones.

Hydrogen bonding in carboxylic acids is even stronger than in alcohols. In fact, carboxylic acid molecules join in pairs called *dimers*. The carboxylic acid structure is uniquely suited to form rings, with two hydrogen bonds between each pair of molecules.

FIGURE 4-4: Hydrogen bonding between carboxylic acid molecules. The dotted lines represent hydrogen bonds.



The -NH_2 , or amino group, like the -OH group, is also capable of hydrogen bonding. However, since nitrogen is less electronegative than oxygen, the bonding is weaker than in compounds containing oxygen.

The effect of hydrogen bonding on the boiling points of alcohols, carboxylic acids, and amines is shown in Table 4-3. Notice that the carboxylic acids have the highest boiling points. The reason is that they form the strongest intermolecular hydrogen bonds. In contrast, the hydrogen bonding in amines is so weak that their boiling points are almost the same as those of the corresponding aldehydes and ketones. Aldehydes and ketones do not form hydrogen bonds. (Question: Why not?) However, their polar character causes dipole-dipole attractions roughly equivalent to the weak hydrogen bonds in amines.

Table 4-3: Boiling Points of Amines, Alcohols, and Carboxylic Acids

	Molecular Mass	Boiling Point $^{\circ}\text{C}$		Molecular Mass	Boiling Point $^{\circ}\text{C}$
ethylamine	45	19	butylamine	73	77
ethanol	46	78	butyl alcohol	74	116
formic acid	46	101	propionic acid	74	140
propylamine	59	49	pentylamine	87	104
propyl alcohol	60	97	pentyl alcohol	88	138
acetic acid	60	118	butyric acid	88	163

ORGANIC SECTION 4-6 FACTORS AFFECTING MELTING POINTS

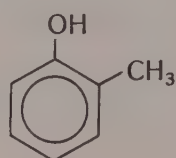
Melting points also depend upon forces of intermolecular attraction. However, melting points are not as simple to analyze as boiling points. The molecules of a solid are closely packed in a regular arrangement. Therefore, the shapes of the molecules play an important role in how well they fit together. The better the fit, the greater the effectiveness of the forces of attraction, and the higher the melting points. Let's look at a few examples.

The effect of molecular geometry on the boiling points of three isomeric pentanes, C_5H_{12} , was discussed in Section 4-3. The melting points of these isomers are:

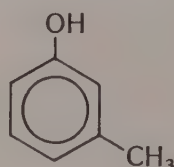
pentane -130°C isopentane -160°C neopentane -17°C

All of these compounds have very low melting points. Of the three isomers, however, neopentane (the one with the lowest boiling point) has the highest melting point. The reason is that neopentane's symmetrical structure enables it to fit together best in the crystal lattice. Isopentane, the isomer with the intermediate boiling point, has the lowest melting point because its molecules have the poorest fit in a crystal lattice. Of the three isomers, the isopentane molecules are the least symmetrical.

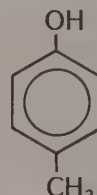
Look at the structural formulas and melting points of three isomeric cresols (methylphenols):



o-cresol
m.p. 31°C



m-cresol
m.p. 11°C



p-cresol
m.p. 35°C

The prefixes *o*, *m*, and *p* refer to *ortho*, *meta*, and *para*. They designate the relative positions of two substituents on a benzene ring. Which cresol molecules do you think would fit together best in the solid crystal structure? Which cresol molecules would you expect to have the poorest fit? Explain in terms of forces of attraction. In disubstituted benzenes such as cresols, the *para* isomer (the most symmetrical) invariably has the highest melting point. Usually, *ortho* isomers have higher melting points than *meta* isomers (the least symmetrical).

It is not always easy to predict melting point trends. The reason is that melting points depend upon both the sizes and shapes of the molecules, and it is not always possible to tell from the structural formula how well the molecules will fit into a crystal.

ORGANIC EXPERIMENT 4-1

USING A PHYSICAL PROPERTY
TO IDENTIFY THE ISOMERS OF DICHLOROBENZENE

Purpose: To use a physical property to identify the *ortho*-, *meta*-, and *para*-forms of dichlorobenzene from three unlabeled samples.

Materials

3 test tubes, 13 mm x 100 mm
1 ringstand and ring
1 Bunsen burner
wire gauze
1 test tube clamp
1 beaker, 250 ml

2 thermometers, -35°C to 50°C
1 thermometer, -10°C to 110°C
samples of *ortho*-, *meta*-, and *para*-
dichlorobenzene, unlabeled
grease pencil (for labeling test tubes)
crushed ice
 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (for ice bath)

Procedure

Your instructor will provide samples of three isomeric dichlorobenzenes, $C_6H_4Cl_2$, but will not tell you which sample is which isomer. Notice that two of the samples are liquids, and that the third is a solid.

1. Obtain three small test tubes. Place about 10 crystals of the solid in a test tube and

- label it A. Place about 10 drops of one of the liquids in a second tube and label it B. Place about 10 drops of the other liquid in the last tube and label it C.
- Place tube A in a beaker containing enough water so that the lower part of the test tube is immersed. Put a thermometer in the test tube. Arrange the beaker, test tube, and thermometer on a wire gauze over a low flame. Use a clamp to hold the test tube. Light the burner and heat the water *slowly*. Stir from time to time and observe the crystals of the solid during the heating. If any change takes place, turn off the burner and allow the water to cool, again stirring the contents of the test tube periodically. Continue to observe whether any changes take place. Record the temperature when, and if, any change occurs.
 - Now put the other two test tubes in another beaker and surround them with a mixture composed of 7 parts finely crushed ice and 6 parts $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$ (by mass). Put a thermometer in each tube. Observe the contents of each test tube, stirring from time to time, as their temperatures are lowered. Note if any changes take place. If any change does occur, remove the test tube from the ice mixture and allow it gradually to warm back to room temperature, again noting any changes taking place. Record the temperature at which any change occurs.

Questions

- What physical property have you determined?
- On the basis of your observations, can you determine which of the three isomers is contained in each test tube? (Use the *Handbook of Chemistry and Physics* to help you answer this question.)

ORGANIC SECTION 4-7 FACTORS AFFECTING SOLUBILITY

Generally speaking, the forces that cause a compound to dissolve (or that prevent it from dissolving) are the same properties that affect boiling points and melting points. However, three separate factors can affect the ability of a substance to dissolve. These are (1) forces between solute molecules, (2) forces between solvent molecules, and (3) forces between solute and solvent.

For example, when butyl alcohol is added to water, some of the alcohol-alcohol and water-water attractions are replaced by alcohol-water attractions. There are enough alcohol-water attractions to dissolve some of the alcohol in water. However, the alcohol-water forces are not strong enough to replace all of the alcohol-alcohol and water-water attractions. As a result, butyl alcohol is *somewhat* soluble in water.

Water is a very effective solvent for polar compounds. Water molecules are polar, and therefore can have dipole-dipole attractions with other molecules. They also can form hydrogen bonds with molecules containing oxygen or nitrogen. Thus, compounds such as acetone that do not form hydrogen bonds with other acetone molecules can undergo hydrogen bonding with water.

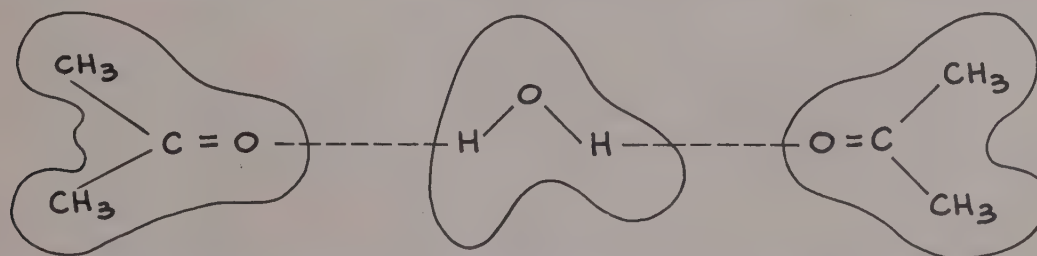


FIGURE 4-5: Hydrogen bonding between acetone molecules and water. The dotted lines represent hydrogen bonds.

“Like Dissolves Like”

The simple rule to follow in predicting solubilities of organic compounds is that “like dissolves like.” This means that the more alike the solvent and solute molecules are in polarity, the more likely it is that the solvent will dissolve the solute. Polar compounds tend to dissolve in polar solvents; non-polar compounds tend to dissolve in non-polar solvents. Water is a very polar solvent. Hydrocarbons are non-polar solvents.

Solubility of Non-Polar Compounds

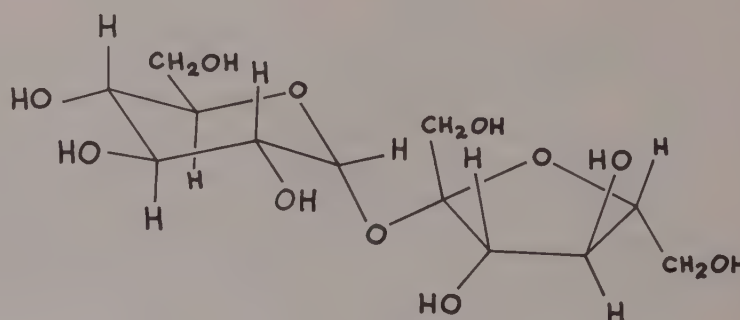
Almost all hydrocarbons are insoluble in water, but quite soluble in non-polar solvents. Halogenated hydrocarbons (alkyl halides) are not sufficiently polar to be very water soluble, but they dissolve very well in non-polar solvents. Compounds with functional groups containing oxygen or nitrogen are soluble in water to varying degrees, depending primarily on how many carbon atoms the molecules have. Such molecules consist of two parts—a polar functional group that tends to dissolve in water, and a non-polar alkyl group that tends not to dissolve in water. If the alkyl group is small (1, 2, or 3 carbon atoms) the polar functional group will be a strong influence, and the compound will tend to dissolve in water. If the alkyl group contains four or more carbon atoms, the two tendencies offset each other and the compound dissolves partially. The solubility in water decreases more and more as the size of the alkyl group increases.

Solubility of Polar Compounds

Compounds with polar functional groups exhibit varying degrees of solubility in non-polar solvents. Generally, as the number of carbon atoms increases, the tendency of the compound with polar functional groups to dissolve in non-polar solvents increases. However, as the molecules become *very* large, the attractions among the solute molecules may become stronger and stronger, and thus it becomes more difficult for the solvent molecules to disrupt the attractions.

Some large molecules may have several polar functional groups. Such molecules may dissolve in water, even though they contain many carbon atoms. For example, consider the case of sucrose (table sugar), $C_{12}H_{22}O_{11}$. The structure of sucrose is rather complicated, but each molecule has eight hydroxyl groups and three ether-type oxygens. These functional groups make sucrose dissolve very easily in water.

FIGURE 4-6: A three-dimensional representation of sucrose.



ORGANIC EXPERIMENT 4-2 TESTING THE SOLUBILITY OF SUCROSE IN VARIOUS SOLVENTS

Purpose: To determine which substances dissolve sucrose.

Materials

1 ml of each of the following solvents:	10 g (approx) sucrose
water	chloroform
ethanol	ethylene glycol dimethyl ether
benzene	glass stirring rod

Procedure

Place a few crystals of sucrose in each of five test tubes. Add about 1 ml of the test solvent to each. Stir the contents of the tubes gently with a glass rod. Record your observations.

Questions

1. In which of the test solvents did sucrose dissolve?
2. Explain your observations in terms of molecular attractions.

SUMMARY, PART FOUR

You have now examined some chemical and physical properties of organic compounds. You have related these properties to functional groups, to distribution of electrical charges that produce polarity and non-polarity, and to the size and shape of molecules. In Parts Five and Six

you will consider how the chemical and physical properties affect the production and function of giant molecules (polymers), and how organic compounds affect the human body.

SUGGESTIONS FOR FURTHER STUDY

1. On a graph, show the relationship between molecular masses and boiling points for the alkanes, ethers, and alkyl chlorides shown in Table 4–1. Plot molecular masses on the horizontal axis and boiling points on the vertical axis. Using separate colors, draw curves for each class of compounds. Do the three curves lie close together? What is the significance of this?
2. Draw the structural formulas for the four isomeric compounds C_4H_9Cl . The boiling points of the isomers are $51^\circ C$, $68^\circ C$, $69^\circ C$, and $79^\circ C$. Which of the four do you think boils at $79^\circ C$? Why are the boiling points of the middle two so close together?
3. On a graph, show the relationship between molecular masses and boiling points for aldehydes and ketones. Use the data from Table 4–2. Draw separate curves for the aldehydes and ketones.
4. On a graph, show the relationship between the molecular masses and boiling points of amines, alcohols, and carboxylic acids. Use the data from Table 4–3. Draw separate curves for each class of compound.
5. Compare the graphs you prepared for questions 1, 3, and 4 (above). What boiling point trends do the graphs show? Can the information of these separate graphs be consolidated onto one graph?
6. The boiling point of diethyl ether is about the same as that of pentane. (See Table 4–1.) Why is diethyl ether, unlike pentane, partially soluble in water?
7. What shape does the neopentane molecule have? To find out, build a model and relate it to methane. Could the name tetramethylmethane be used as a name for neopentane? For pentane?
8. Piaget, a famous child psychologist, used a piece of Plasticine to test a child's concept of the conservation of matter. Obtain a piece of modeling clay and use it to investigate how many different shapes you can produce with the same bit of matter. As you do so, study the surface area and determine how it changes with the shape.

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Detailed information about the chemical and physical properties of both organic and inorganic molecules.
- Paul, Iain C., and David Y. Curtin, "Reactions of Organic Crystals with Gases," *Science*, January 10, 1975, p. 19.
By studying the degree of reactivity between a gas and various crystals, insights into the crystalline structure can be gained. Excellent diagrams clarify differences in crystal structure.
- Thomson, Tom R., *Chemistry: Introduction to Matter*, Addison-Wesley Publishing Co., Menlo Park, Calif., 1973.
In Chapter 3 ("The States of Matter"), changes from solid–liquid–gas are explained in terms of energy. Chapter 7 ("The Changes that Matter Undergoes") reviews principles of physical and chemical changes. Chapters 25 and 26 focus on organic chemistry. Chapter 27 is devoted to biochemistry.

PART FIVE GIANT MOLECULES: POLYMERS

OBJECTIVES

When you have finished Part Five, you will be expected to demonstrate acceptable performance on the following learning objectives:

1. Describe the relationship between monomers and polymers.
2. Describe and illustrate addition polymerization

3. Describe and illustrate condensation polymerization.
4. Describe three methods used by chemists to control the process of polymerization.
5. Compare the properties of two natural and two synthetic polymers.
6. Explain the functions of natural polymers in living organisms, and relate these functions to the properties of the polymers.
7. Describe the relationship between sugars, starch, and cellulose, and explain the differences in their properties in terms of the differences in their structures.
8. Define amino acids by writing a generalized structural formula, and describe the relationship of amino acids to proteins.
9. Describe the hydrolysis of starch and state its relationship to condensation polymerization.
10. Relate the functions of DNA and RNA to their structures.
11. Relate the preparation of polymers to the chemistry of the functional groups studied in Part Three.

INTRODUCTION

Saran, nylon, Teflon. Carbohydrates, proteins, nucleic acids. Resins. Rubber, polyesters. What do all these natural and synthetic materials have in common? They are all *polymers*. In fact, polymers may be the most important organic molecules of all. Even the human body is constructed primarily of polymers. If all polymers were removed from your body, nothing would be left except a pool of water containing a few inorganic salts and organic compounds. In this part of the module, we will examine some important natural and synthetic polymers.

ORGANIC SECTION 5-1 MONOMERS AND POLYMERS

What is a polymer? A polymer can be compared to a chain-link fence. A chain fence is made up of individual links joined together. Similarly, many large molecules (often called macromolecules) are composed of smaller units, called *monomers*, linked together by chemical bonds. The combination of hundreds, thousands, or even millions of monomers produces a *polymer* (from Greek, *poly*=many, *meros*=parts).



Some of the most complex polymers have existed in nature for millions of years. These natural polymers are the building blocks of living things, and therefore are essential for life. Carbohydrates, proteins, nucleic acids, rubber, and many resins are natural polymers. Cellulose, a carbohydrate polymer, is the structural backbone of plants. Proteins, polymers of amino acids, have a variety of functions in all living organisms. The nucleic acids—DNA and RNA—are the polymers responsible for heredity.

The developments in synthetic polymer chemistry over the last 30 years or so have had an enormous impact on modern society. Synthetic polymers are found everywhere. We wear them; we eat from them; we brush our teeth with them; we store garbage in them; and we use countless objects each day which are manufactured from them, such as telephones, phonograph records, television sets, auto parts, toys, tools, and kitchen utensils. There is no escaping synthetic polymers. Some of the familiar synthetic polymers are Saran, nylon, Orlon, Lucite, melamine, acrylic, and Bakelite.

Natural and synthetic polymers are divided into two groups—addition polymers and condensation polymers, depending on the type of polymerization reaction used to produce them.

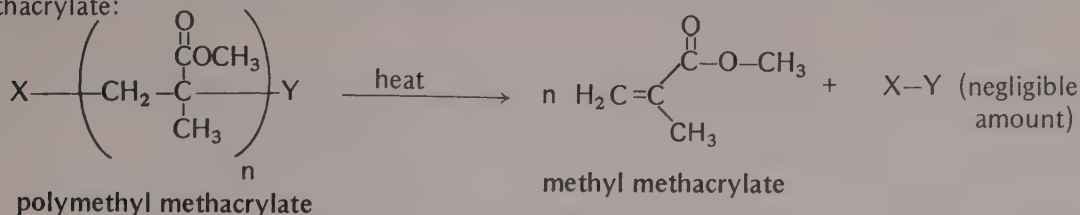
Table 5-1: Addition Polymers

Monomer	Name	Structure	Uses	Characteristic Properties
$\text{CH}_2=\text{CH}_2$	polyethylene	$\left(\text{CH}_2-\text{CH}_2\right)_n$	kitchenware, bags, containers, sheets, pipes, toys	translucent; waxy-looking; softens at about 85°C
$\text{CH}_2=\text{CH}-\text{CH}_3$	polypropylene	$\left(\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}\right)_n$	kitchenware, bottles, containers, lab ware, fibers, films, carpets	more flexible than polyethylene; softens at about 120°C
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$	polystyrene Styrofoam	$\left(\text{CH}_2-\underset{\text{C}_6\text{H}_5}{\text{CH}}\right)_n$	insulation, packing, furniture, household articles, picnic coolers	thermoplastic; softens at about 90°C ; can be prepared as a foam
$\text{CH}_2=\text{CH}-\text{Cl}$	polyvinyl chloride PVC	$\left(\text{CH}_2-\underset{\text{Cl}}{\text{CH}}\right)_n$	lacquer, phono records, plumbing, vinyl leather, fabric coating for raincoats, upholstery	hard and tough; monomer hazardous to health
$\text{CH}_2=\text{CH}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	polyvinyl acetate	$\left(\text{CH}_2-\underset{\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3}{\text{CH}}\right)_n$	coatings adhesives perma press safety glass	very low softening point; cannot be molded; clear, glassy
$\text{CH}_2=\text{CH}-\text{OH}$	polyvinyl alcohol	$\left(\text{CH}_2-\underset{\text{OH}}{\text{CH}}\right)_n$	water-soluble packages water thickener adhesive	soluble in water; crystalline fiber
$\text{CH}_2=\underset{\text{CH}_3}{\overset{\text{O}=\text{C}-\text{O}-\text{CH}_3}{\text{C}}}$	polymethyl methacrylate	$\left(\text{CH}_2-\underset{\text{CH}_3}{\overset{\text{O}=\text{C}-\text{O}-\text{CH}_3}{\text{C}}}\right)_n$	windshields, canopy bubbles, latex paints, Lucite, Plexiglass, Perspex	highly transparent; high index of refraction
$\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$	polyacrylonitrile	$\left(\text{CH}_2-\underset{\text{C}\equiv\text{N}}{\text{CH}}\right)_n$	fabrics Orlon Acrilan ¹	stable to outdoor exposure, solvents, and acids; fibers similar to wool, silk
$\text{F}-\underset{\text{F}}{\overset{\text{F}}{\text{C}}}=\underset{\text{F}}{\overset{\text{F}}{\text{C}}}-\text{F}$	polytetrafluoroethylene	$\left(\text{CF}_2-\text{CF}_2\right)_n$	cookware, bearings, Teflon	stable at high temperatures; insoluble in most solvents
$\text{H}-\underset{\text{H}}{\overset{\text{Cl}}{\text{C}}}=\underset{\text{Cl}}{\text{C}}-\text{H}$	polyvinylidene chloride	$\left(\text{CH}_2-\underset{\text{Cl}}{\overset{\text{Cl}}{\text{C}}}\right)_n$	packaging wrapping Saran ²	transparent

¹ A copolymer of acrylonitrile and vinyl acetate² A copolymer of vinylidene chloride and vinyl chloride

ORGANIC EXPERIMENT 5-1 POLYMERIZATION AND DEPOLYMERIZATION

Some polymerization reactions can be reversed by strongly heating the polymer. For example, polymethyl methacrylate (Plexiglas, Lucite) can be depolymerized to the monomer methyl methacrylate:



In this experiment, you will first depolymerize polymethyl methacrylate, and then re-form the polymer.

Purpose: To observe the depolymerization of the polymer polymethyl methacrylate, and the polymerization of the monomer methyl methacrylate.

Materials

5 g granulated polymethyl methacrylate	Bunsen burner
1 test tube, 18 mm x 150 mm	1 beaker, 250 ml
4 test tubes, 13 mm x 100 mm	ice
3 corks to fit 13 mm x 100 mm test tubes	1 crystal of hydroquinone
8 mm glass tubing with right-angle bend	2 to 3 drops of methyl ethyl ketone peroxide solution (MEK peroxide, an initiator)
1 one-hole stopper to fit 13 mm x 100 mm test tube	dropper bottle containing solution of 0.1M Br_2 in CCl_4
2 ringstands and 2 clamps	

Procedure

1. Place 5 g of granulated polymethyl methacrylate in an 18-mm x 150-mm test tube. Mount a piece of 8-mm glass tubing, with a right-angle bend, through a stopper in the test tube. Clamp the test tube at a 45° angle, as shown. (See Figure 5-2.) Insert the other end of the glass tube into a 13-mm x 100-mm test tube. Surround the second test tube with an ice-water mixture.
2. Heat the tube containing the polymer with a small, luminous flame from a Bunsen burner held in your hand. Keep the flame rotating as the polymer gradually softens. When about 1 ml of liquid has appeared in the second tube, discontinue the heating.
3. Pour part of the liquid from the second tube into three other 13- x 100-mm test tubes, so that you have four samples of the liquid. Test one sample with a solution of bromine in carbon tetrachloride. (See Experiment 2-5, page 19.) To the second sample add a minute crystal

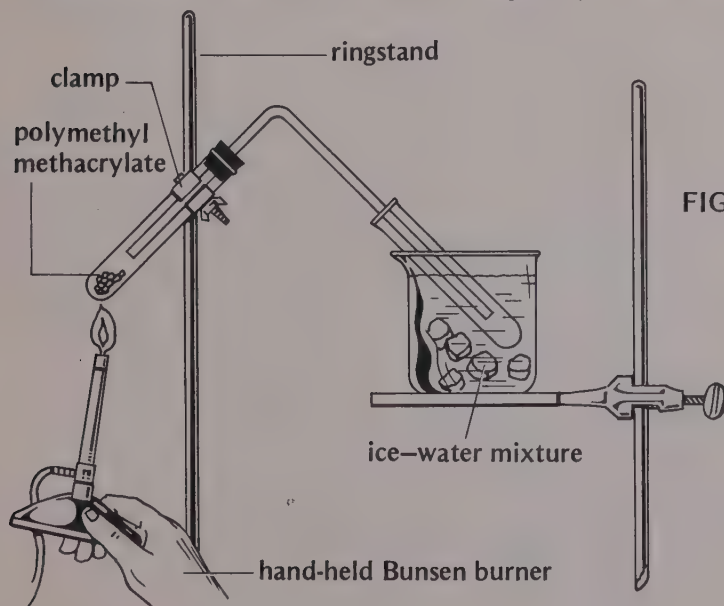


FIGURE 5-2: Laboratory setup for Experiment 5-1.

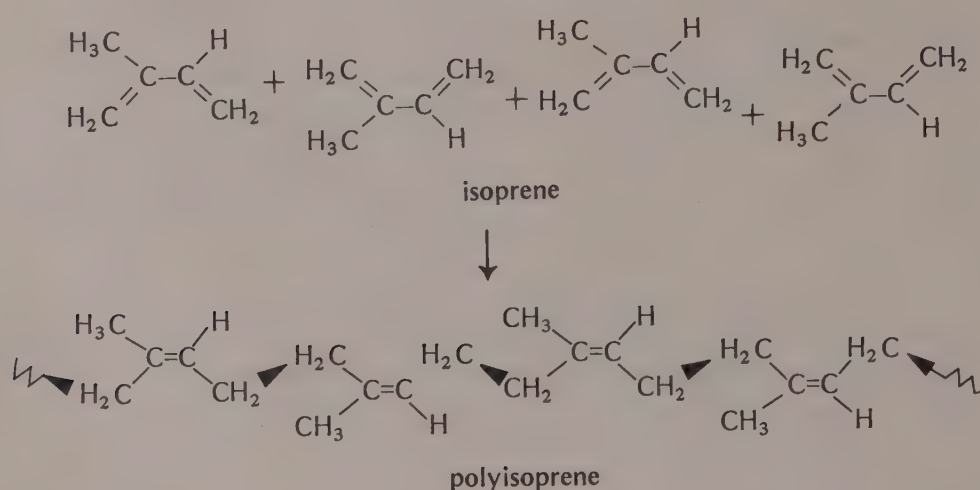
of hydroquinone. To the third add 2 to 3 drops of MEK peroxide solution. (See page 45.) Add nothing to the fourth. Cork the last three tubes tightly and expose to sunlight for several days. Observe them from time to time and describe any changes you see. Record your observations.

Questions

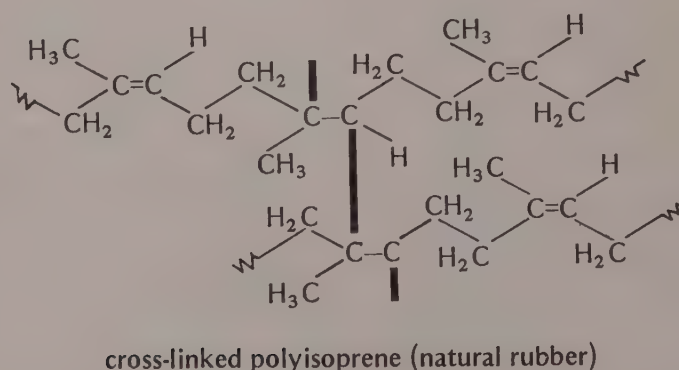
1. What chemical reaction did you bring about by heating the polymer?
2. What do you conclude from the test with bromine?
3. What is the function of hydroquinone in this experiment?
4. What is the function of M.E.K. peroxide in this experiment?
5. Is methyl methacrylate reactive enough to undergo polymerization without an initiator?

Natural and Vulcanized Rubber

Rubber is a naturally-occurring addition polymer of isoprene (2-methyl-1,3-butadiene). Unlike the vinyl monomers, isoprene has *two* double bonds. During polymerization, addition occurs at the two ends of the four-carbon chains of the diene molecules (sometimes called 1,4-addition). As the new bonds form at each end of the diene molecules, double bonds develop in the middle of each monomer unit.



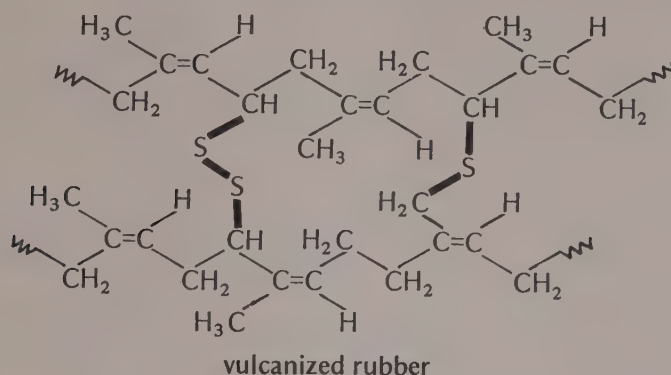
Since polyisoprene molecules still contain double bonds, additional polymerization can take place, with the resulting formation of cross links between polymer chains. Many of the double bonds, however, remain.



Cross-linked polyisoprene is *natural rubber*, a soft, sticky, somewhat elastic substance. It becomes hard and brittle when cooled. The molecules have long, flexible chains which do not attract one another very strongly. The van der Waals attractions are weak because the geometry of the molecules does not permit them to fit closely together. Also, the molecules are non-polar,

so there are no other attractions. As a result rubber is an amorphous material whose randomly-oriented molecules are not carefully oriented as they would be in a crystalline solid. When rubber is stretched, the chains are straightened out somewhat, and they become oriented in a more orderly fashion. But once the stress is released, the rubber returns to its amorphous form because there are no intermolecular forces to keep it stretched. The few cross links between chains prevent them from sliding past one another, and thus the rubber has some elasticity.

The properties of natural rubber can be altered by heating it with sulfur—a process called *vulcanization*. The sulfur atoms form additional cross links between polyisoprene chains, forming a harder, stronger, more elastic material.

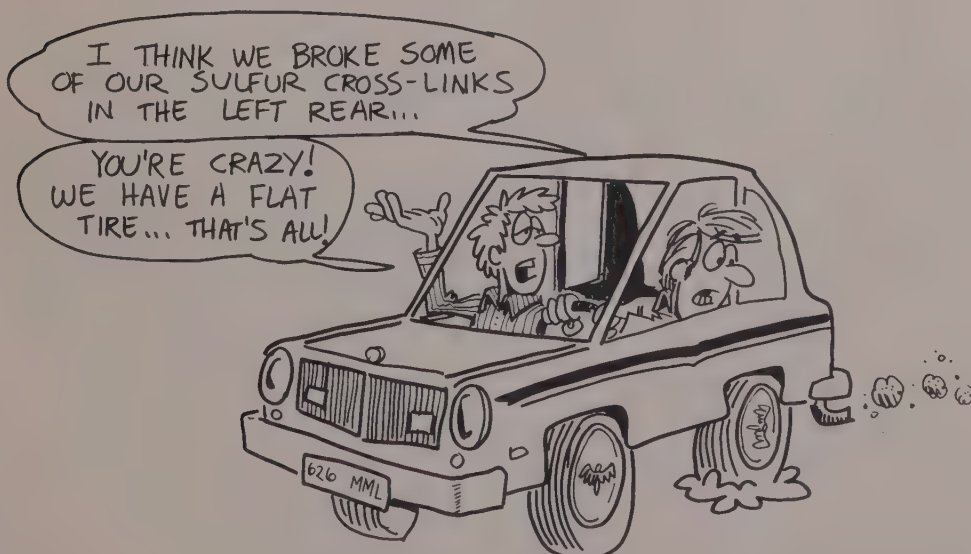


Old Plastics Never Die...

One of the biggest problems brought about by the abundance of synthetic polymers is getting rid of them. The durability of plastics—one of the properties that makes them so useful—makes them virtually impossible to dispose of. They resist chemical breakdown because they are very inert. Burning them can create serious air pollution. Burying them only gets them temporarily out of sight, since they are not biodegradable, as natural polymers are. Two obvious ways to cut down on the waste problem would be recycling and eliminating the unnecessary use of plastics for packaging. Can you suggest some other solutions?

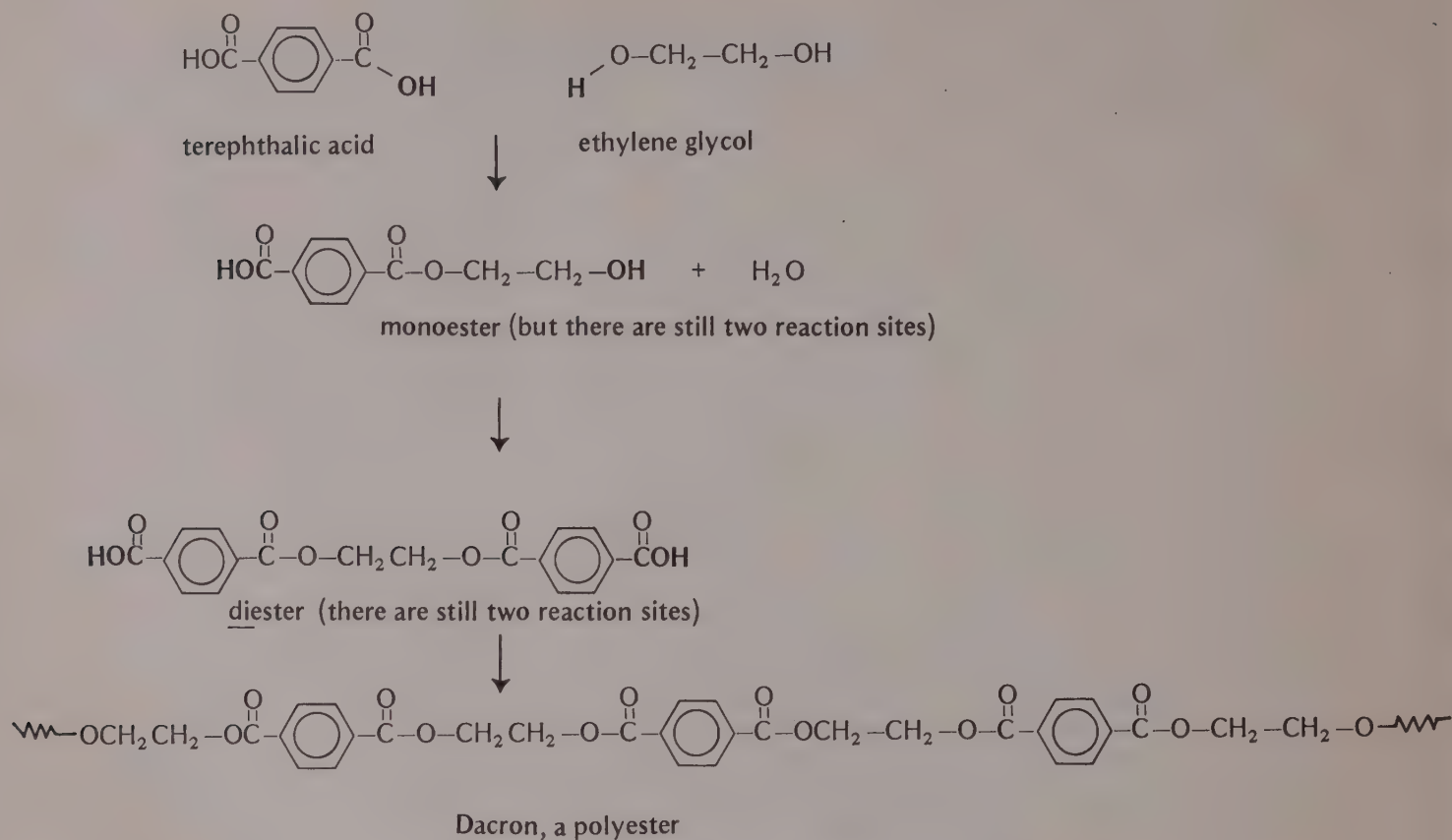
ORGANIC SECTION 5-3 CONDENSATION POLYMERS

Condensation polymerization differs from addition polymerization in two ways. First, when the monomer units are joined together in a condensation polymerization, a small molecule—for example, H_2O , NH_3 , or HCl —is split off as a by-product. Second, each monomer unit contains two or more functional groups at which condensation can occur. The functional groups on any monomer may be the same, or they may be different.

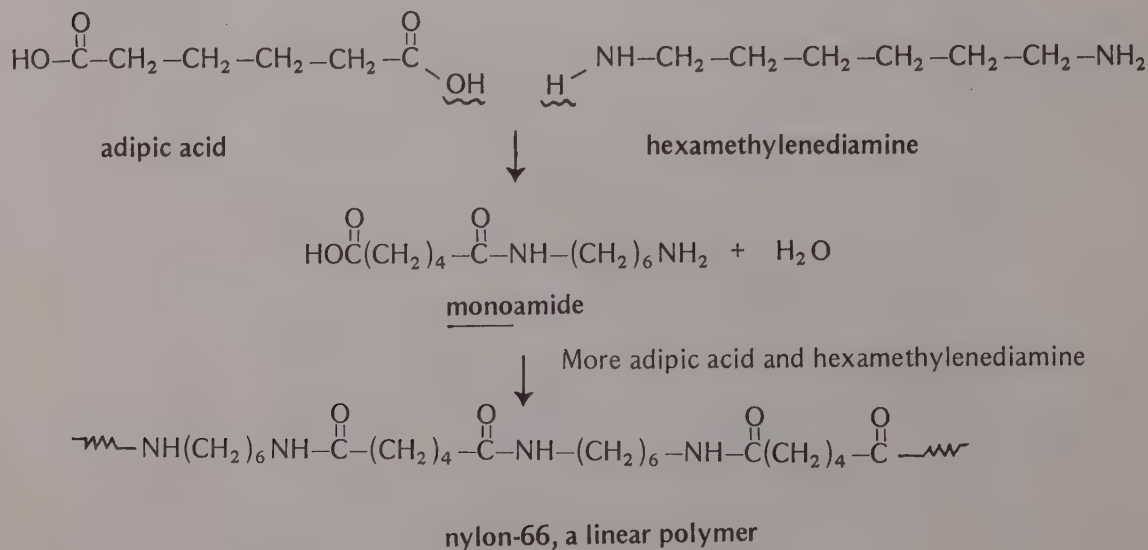


Some Synthetic Condensation Polymers: Polyesters and Nylons

An example of a synthetic condensation polymerization is the formation of the polyester fiber, Dacron. Terephthalic acid and ethylene glycol, a dicarboxylic acid and di-alcohol respectively, can each react at two sites. They condense to form the polyester, Dacron, as shown below:



Dacron is one of many synthetic polyester compounds. Polymers can also be made from compounds containing an *amide* link, $\text{—}\overset{\text{O}}{\parallel}\text{C—NH—}$. Nylon, a polyamide, was first synthesized in 1940 to replace silk in clothing and parachutes. As is often the case “necessity is the mother of invention”—nylons were developed after we had been cut off from the major silk suppliers at the beginning of World War II. (What other major chemical breakthroughs with significant peacetime uses came as a result of war?) The formation of nylon-66, a copolymer of adipic acid and hexamethylenediamine, is shown below. Note once more how the polymer grows at both ends:



Nylon threads are produced by melting the polymer and extruding it through tiny holes to make filaments. The polymer molecules in the filaments are aligned by this process of stretching. The resulting fibers have great tensile strength.

ORGANIC EXPERIMENT 5-2

SYNTHESIS OF NYLON-66

Purpose: To synthesize nylon-66, a condensation polymer.

Materials

2 beakers, 100 ml

solutions of each of the following:

1 ml adipyl chloride in 25 ml cyclohexane

1 ml hexamethylenediamine (1,6-hexanediamine)
in 25 ml H₂O

6 M NaOH in dropper bottle

10-cm length of copper wire

1 test tube, 18 mm x 150 mm

25 ml ethanol or acetone

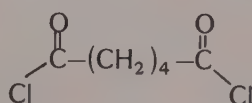
Procedure

In a 100-ml beaker place a solution prepared by dissolving 1 ml of adipyl chloride in 25 ml of cyclohexane. In a second beaker place a solution of 1 ml of hexamethylenediamine (1,6-hexanediamine) in 25 ml H₂O, and add a few drops of 6 M sodium hydroxide. Tilt this beaker slightly, and carefully pour the solution of adipyl chloride down the inside wall of the first beaker so that two layers are formed. Avoid any motion that might mix the two solutions. Note the film formed at the liquid-liquid interface. Form a hook at the end of a piece of copper wire. Use the hook to catch the film at the interface. Slowly pull the wire from the beaker, pulling along with it a continuously forming nylon rope. As the rope is pulled from the solution, you can wind it onto a spool (a test tube makes a good spool).

When the strand breaks, wash it with water, then with ethanol or acetone, and let it dry.

Questions

1. Examine and describe the properties of the polymer you have produced. Is it like the nylon you are used to? Could you make a shirt or dress from it, or is it too brittle?
2. Why is it important that the solutions of the two reactants be immiscible? What do you suppose would be the result if the acid chloride were dissolved in a solvent that is miscible in water instead of a hydrocarbon solvent?
3. The formula for adipyl chloride is shown below. Write an equation for the reaction of adipyl chloride and hexamethylenediamine to form nylon-66.



adipyl chloride

4. What is the small-molecule by-product of the reaction described in Question 3? (*Hint:* It's not water.) What is the role of the sodium hydroxide?

Suggestions for Further Study

You can improve the properties of nylon-66 prepared in this experiment by heating it to just below its melting point, then stretching it. Fibers are made of molecules. The molecules in your nylon sample are randomly oriented. When the fibers are stretched, the molecules become aligned in parallel rows. Once aligned, stronger hydrogen bonding occurs. Hence, nylon fibers are stronger when the molecules are stretched.

ORGANIC SECTION 5-4 PROTEINS: NATURAL CONDENSATION POLYMERS

Polyesters and nylons are important synthetic condensation polymers. But although these synthetic polymers certainly are useful, they cannot compare in importance with some of the *natural* condensation polymers—proteins, carbohydrates, and nucleic acids.

Proteins and nylons are similar: they are both polyamides. In Experiment 5-2, you synthesized nylon, a polyamide polymer. Proteins, one group of natural polyamides, might well be called the "stuff of life". They are found in all living cells. For example, proteins are the chief components of muscles, nails, hair, wool, silk, and egg whites. Enzymes, antibodies, hemoglobin, albumin, and many hormones are also proteins.

Amino Acids

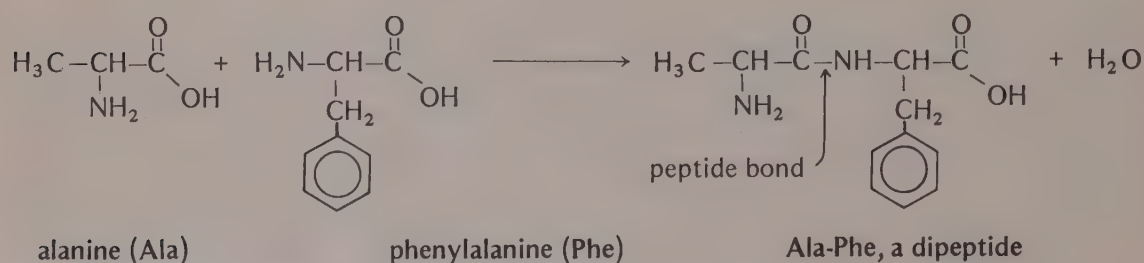
The monomer units for proteins are α -amino acids, which are carboxylic acids with an amino group attached to the α carbon (the carbon next to the carboxyl group). Twenty-six amino acids are commonly found in nature. Structures for a few amino acids are shown in Table 5-2.

Table 5-2: Structural Formulas of a Few Amino Acids

$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{C}-\text{C} \\ \\ \text{NH}_2 \\ \text{OH} \end{array}$ <p>glycine (Gly)</p>	$\begin{array}{c} \text{H} \quad \text{O} \\ \quad \parallel \\ \text{H}_3\text{C}-\text{C}-\text{C} \\ \quad \\ \text{NH}_2 \quad \text{OH} \end{array}$ <p>alanine (Ala)</p>	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \\ \quad \quad \parallel \\ \text{C}_6\text{H}_5-\text{C}-\text{C}-\text{C} \\ \quad \\ \text{H} \quad \text{NH}_2 \\ \text{OH} \end{array}$ <p>phenylalanine (Phe)</p>
$\begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \\ \quad \quad \parallel \\ \text{HO}-\text{C}-\text{C}-\text{C} \\ \quad \\ \text{H} \quad \text{NH}_2 \\ \text{OH} \end{array}$ <p>serine (Ser)</p>	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \\ \quad \quad \parallel \\ \text{HS}-\text{C}-\text{C}-\text{C} \\ \quad \\ \text{H} \quad \text{NH}_2 \\ \text{OH} \end{array}$ <p>cysteine (Cys)</p>	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \\ \quad \quad \parallel \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{C} \\ \quad \\ \text{CH}_3 \quad \text{NH}_2 \\ \text{OH} \end{array}$ <p>valine (Val)</p>

Peptide Bonds

A *dipeptide* is formed when two amino acids are joined together by a *peptide bond*:



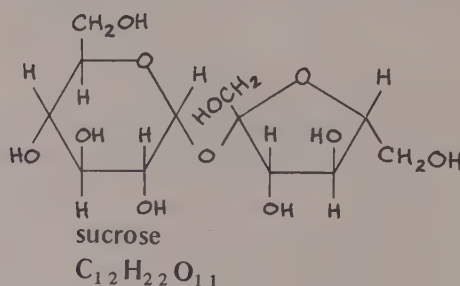
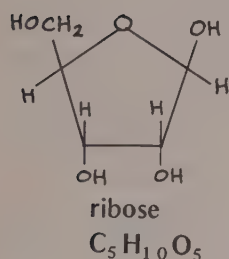
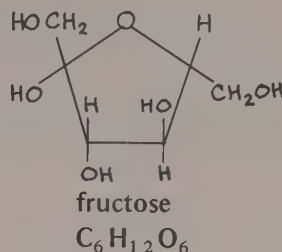
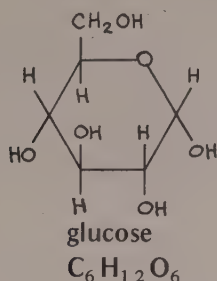
Notice that the formation of the peptide bond is a *condensation* reaction: each amino acid has two functional groups at which condensation can occur ($-\text{NH}_2$ and $-\text{COOH}$), and water is split off as a by-product of the condensation. The peptide bond is an amide link just like the one in nylon. Usually, amino acid polymers with molecular masses under 5000 (about 35 to 50 amino acids) are called *polypeptides*. Larger polypeptides are called *proteins*. Insulin, a relatively small protein whose molecular mass is about 6000, contains 51 amino acid units.

Natural polypeptides and proteins play very specific roles. Each has a unique structure. Each has a *primary structure*, which is determined by the number of amino acids and their sequence. For example, the tetrapeptide Ala-Ser-Val-Gly and Ala-Gly-Val-Ser are different from each other (the order of amino acids is different). Both of these sequences differ from the pentapeptide Ala-Ser-Val-Gly-Ser (the number of amino acids is different).

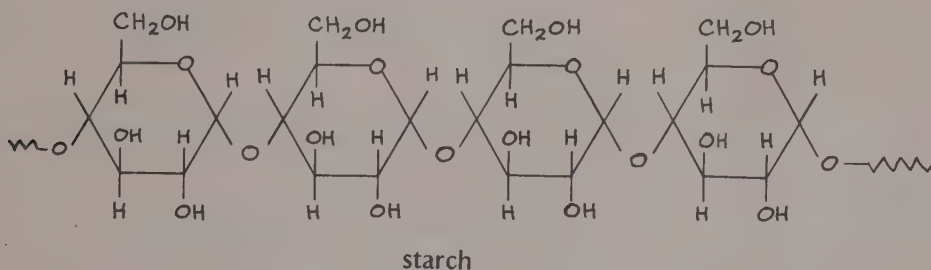
In addition to their primary structure, many natural polypeptides and proteins have a specific *secondary structure*—that is, they are stretched side-by-side, or coiled or folded in very specific ways. Disruption of the secondary structure of a protein will often destroy its biological activity, which means that the protein will no longer function as it should. The secondary structure of a protein can be affected by heating it, by changing the pH of its environment, or by changing the polarity of its surroundings.

ORGANIC SECTION 5-5 CARBOHYDRATE POLYMERS: STARCH AND CELLULOSE

Many carbohydrates are natural condensation polymers with the general formula $C_x(H_2O)_y$. Early chemists thought these compounds were hydrates of carbon, which is why they were named carbohydrates. We now realize that these naturally occurring compounds are polyhydroxy compounds. Glucose, fructose (a sugar found in natural substances like honey), sucrose (table sugar, composed of glucose and fructose bonded together), and ribose (a five-carbon sugar present in nucleic acids) are all simple carbohydrates.

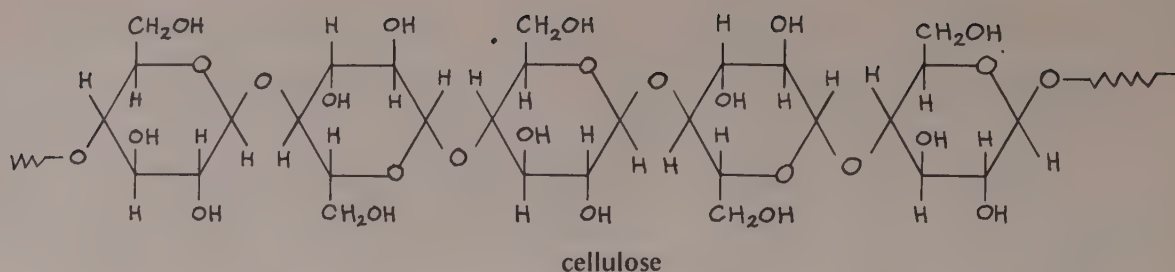


In Section 1-3 you read that the oxidation of glucose to CO_2 and H_2O supplies energy for your body. However, we consume very little glucose directly. Most of the glucose our bodies use comes from starch, a giant condensation polymer of glucose. A number of foods we eat regularly—potatoes, corn, wheat (breads and cereals), and rice—are excellent sources of starch.



In living organisms starch is separated by enzymes into glucose, which is either oxidized for energy or stored as the polymer glycogen. The process by which starch is broken down to glucose is called *hydrolysis*. Hydrolysis is the process of separating the parts of a molecule by adding water. It is the reverse of the condensation reaction for forming polymers.

Cellulose is a glucose polymer synthesized by plants. In plants, starch serves as the reserve food supply, and cellulose serves as the structural matter. It gives plants their stiffness and shape. Wood, once the water is removed, is about 50 percent cellulose; cotton is almost all cellulose. The only difference between starch and cellulose is the geometry of the oxygen link between the glucose units. This small difference is sufficient to make cellulose unusable as a food for man and most animals. Most animals do not produce the appropriate enzymes needed to break down cellulose into useful food materials. However, cud-chewing animals (called ruminants) and termites do use cellulose as a food.



Even though we don't use the cellulose we eat as a nutrient, we do use it in other ways. The uses of wood and cotton are well known. Wood pulp is used to produce paper and a number of other products, and it is a major source of pure cellulose. Cellulose can be chemically altered to make celluloid, the first commercial plastic (patented in 1869). Cellulose is also used for cellophane, rayon, and a large number of other plastics and fibers.

ORGANIC EXPERIMENT 5-3 HYDROLYSIS OF STARCH

Purpose: To observe the hydrolysis of starch to glucose.

Materials

2 test tubes, 13 mm x 100 mm	1 stirring rod
4 test tubes, 18 mm x 150 mm	aqueous iodine solution in dropper bottle
1 g of sucrose and glucose	1 ringstand and ring
NaOH pellets	wire gauze
1 test tube holder and rack	1 beaker, 1000 ml
1 Bunsen burner	4 ml dilute HCl
1 g household starch in 25 ml water	

Procedure

PART I: HYDROLYSIS OF STARCH

- Shake 1 g of household starch (the kind that dissolves instantly) in about 25 ml of water. Divide this solution equally among four numbered 18-mm x 150-mm test tubes. Add 2 ml of dilute HCl to tubes 1 and 3, and then heat all the solutions to boiling for a full five minutes. Set tubes 1 and 2 adjacent to one another, and 3 and 4 adjacent to one another.
- Add two pellets of NaOH to tubes 1 and 2 while the solutions are still hot, and stir each tube with a glass rod to dissolve the solid. Allow the solutions to cool for several minutes. Compare the tubes, and record your observations.
- Allow tubes 3 and 4 to cool to room temperature—about ten minutes. Add 5 drops of aqueous iodine solution to each test tube. Compare the tubes, and record your observations. Can you explain what happens in each case?

PART II: DISTINGUISHING A FREE SUGAR FROM A POLYMERIZED SUGAR

Half fill two 13-mm x 100-mm test tubes with water, and bring them to just under boiling. Place a pinch of sucrose in one and a pinch of glucose in the other. Drop a pellet of NaOH into each tube, and allow them to cool for several minutes. **CAUTION:** Do not bring NaOH pellets into direct contact with your skin. Compare the tubes, and record your results. (*Note:* Free sugars will cause the solution to turn yellow, then brown. Some sugars bound to other sugars will not exhibit a color change because the bond ruptures responsible for the color change do not occur.)

Questions

- Based on your observations of what happened in Part I, which of the tubes contained a free sugar? How do you know?
- Using structural formulas, write the reaction that occurs when sucrose is hydrolyzed to glucose and fructose.
- In Part I, what is the iodine a test for?
- Write an equation showing the hydrolysis of starch $(C_6H_{10}O_5)_n$ to glucose. (*Note:* The acid acts as a catalyst.)

ORGANIC SECTION 5-6 NUCLEIC ACIDS: DNA AND RNA

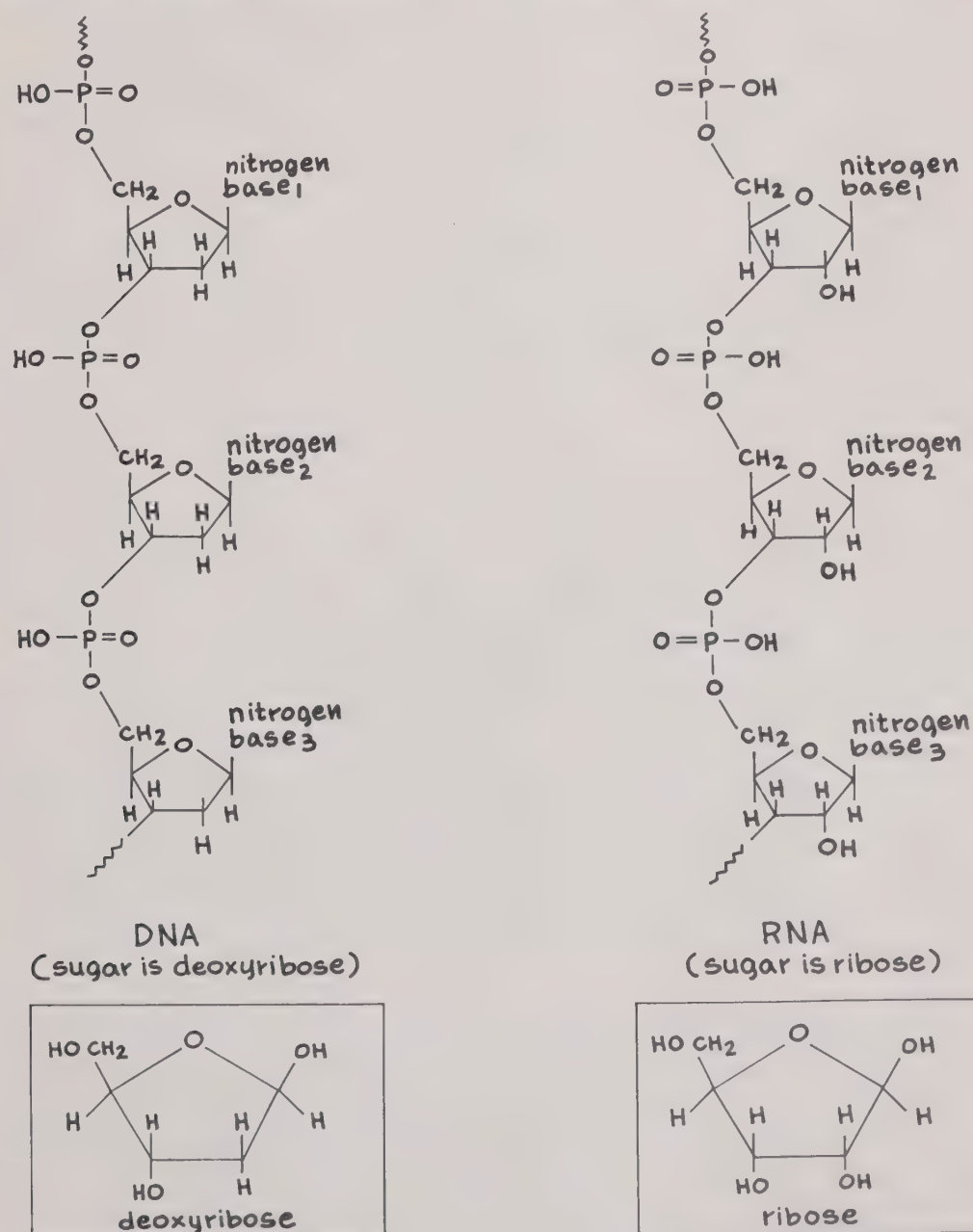
Among the most important natural condensation polymers are the *nucleoproteins*, large molecules made up of *nucleic acids* attached to proteins. Nucleoproteins are found in the cells of all organisms, and as the name *nucleoprotein* suggests, these molecules are found in the cell nucleus. Nucleoproteins make up large structures called *chromosomes*, long known to play a role in cell division. The chromosomes carry coded information which, when translated, directs all the activities that occur within the cell, including metabolism, protein synthesis, and reproduction. The coded information is carried by the nucleic acid part of the nucleoprotein—specifically, by *DNA* (*deoxyribonucleic acid*) which carries the instructions for the synthesis of specific proteins. Another nucleic acid, *RNA* (*ribonucleic acid*) also plays a role in protein synthesis.

In addition to carrying the instructions for synthesizing proteins, DNA also transmits the code to new cells. When new cells are formed (or, for that matter, when new individuals are born) each must be supplied with a complete set of instructions for later development. All of these instructions are carried by the nucleic acid polymers.

Nucleic Acid Components: Phosphate Groups, Sugars, and Nitrogen Bases

Nucleic acids are copolymers composed of a phosphate group and a sugar. (See Figure 5-4.) In the case of DNA the sugar is deoxyribose; in RNA the sugar is ribose.

FIGURE 5-4:
Backbone structures
of DNA and RNA.



The monomer unit for the nucleic acid polymer is the *nucleotide*, which is composed of phosphate, a sugar and a nitrogen base. Four nitrogen bases appear in DNA. They are adenine (A), guanine (G), cytosine (C) and thymine (T). A fifth base, uracil (U), is present in RNA instead of thymine.

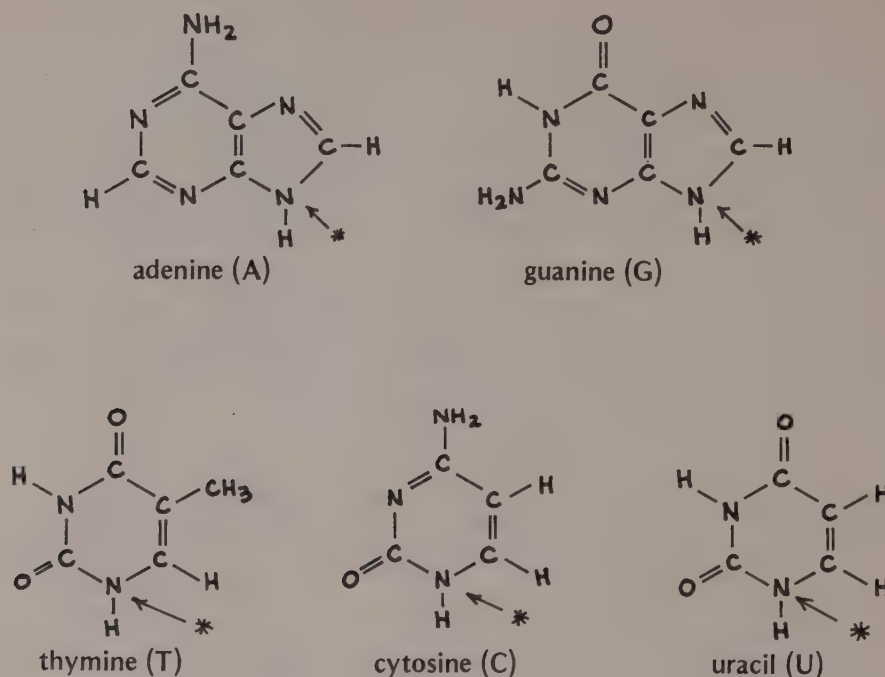


FIGURE 5-5: The five nitrogen bases found in nucleic acids. The arrows indicate where each base bonds with its sugar.

The Code

DNA is a polymer composed of four nucleotides. The nucleotides differ from one another only in the identity of the nitrogen bases. Scientists now know that it is the *sequence*, or order, of nitrogen bases in the DNA molecule that determines the protein that will be synthesized. You read in section 5-4 that proteins are composed of specifically ordered strands of amino acids. Moreover, the sequence of nucleotides in the DNA molecule determines the sequence of amino acids in the proteins the DNA produces. Biologists and chemists have succeeded in "breaking the code" for DNA. They have learned that a sequence of three nitrogen bases stands for an amino acid. For example, the DNA code sequence CCA stands for the amino acid glycine. The sequence CAA, on the other hand, stands for valine. Each amino acid is represented by its own three-nucleotide sequence on the DNA molecule. During the process of protein synthesis, the DNA nitrogen-base sequences are read from one end to the other, and as a result amino acids are assembled in a specific order. The result is that cells are able to produce thousands of specific proteins.

The Double Helix

DNA actually exists as a *double strand* of nucleotide units. The two strands are twisted around one another to form a double helix. (See Figure 5-6.) The helix has the sugar-phosphate backbone on the outside, and the bases point in toward one another. The double helix is like a spiral staircase, in which the base pairs serve as steps. The two chains are held together by hydrogen bonds between the bases. One crucial aspect of the double-helix configuration is that the two chains are not intertwined randomly. Instead, the bases are paired with one another. For example, whenever guanine appears on one strand of the helix, cytosine is just opposite it on the other

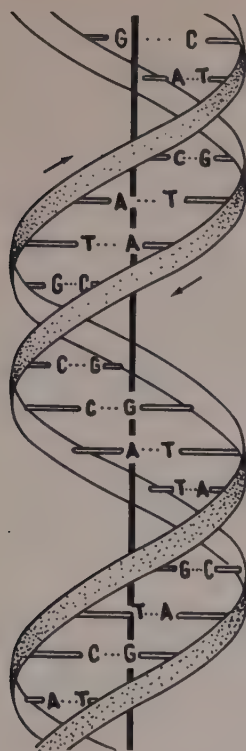


FIGURE 5-6:

A fragment of the DNA double helix. The dotted lines represent hydrogen bonds between paired bases.

strand. Whenever adenine appears on one strand it is always paired with thymine on the other strand. The two strands are said to be *complementary*. They are not twins of one another, but if you know the sequence of nucleotides on one strand, you also know the nucleotide sequence on the other strand.

The process by which nucleic acids actually direct the synthesis of proteins has only recently been understood. Unfortunately, the details of the process are too complicated to be described here. However, the story of DNA and RNA action, along with the description of the discovery of the structure and function of the nucleic acids, makes fascinating reading. Consult the references in the *Bibliography* (page 58) for sources of more information on these topics.

SUMMARY, PART FIVE

Polymers provide numerous examples of functional groups in action. The study of synthetic polymers is an active branch of organic chemistry. Polymer chemists continually strive to make molecules with new sets of useful properties. One of the greatest priorities is the development of useful polymers which are biodegradable, rather than virtually indestructible, as are many in current use.

The study of natural polymers, including their production and their functions in living organisms, comprise the intersection of biology and chemistry known as *biochemistry*. Biochemical research adds to our understanding of life processes, and it has helped us find ways to control and eliminate many medical problems. Even cancer may someday be better understood as a result of biochemical research. Biochemistry also provides insight into the physiological effects of various substances used by people as medicines and as drugs.

SUGGESTIONS FOR FURTHER STUDY

1. Consider possible ways to dispose of plastic waste materials. Do some research to determine how difficult it will be to develop biodegradable plastics. Try to think of and test other methods of plastic disposal.
2. Make a collection of as many different plastics as you can. Then, devise an experiment to test the chemical and physical properties of your collection.
3. What characteristics will a plastic substance have if all the bonds connect the basic units together in a rope-like fashion?

4. What characteristics will a plastic substance have if the bonds connect basic units into a two-dimensional bonding network?
5. What characteristics will a plastic substance have if the bonds connect basic units into a three-dimensional bonding network?
6. Identify plastics which have the properties you have identified for items 3–5. Do they have the bonding networks that you expected?
7. What advantages and disadvantages can you identify for thermosetting plastics?
8. What advantages and disadvantages can you identify for thermoplastic substances?
9. How do amino acids polymerize?
10. Where does DNA fit into the process of polymerizing amino acids?
11. Neoprene is sometimes used in place of natural rubber. Neoprene is formed by a polymerization reaction. Do some research to find out how neoprene is made and how it is used.

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Anon., "Enzymes and Aging," *Chemistry*, September, 1973, p. 21.

One theory of aging says that faulty enzymes produce damaged proteins. The enzyme aldolase is twice as active in young as in old mice.

Moore, John W., "The Vinyl Chloride Story," *Chemistry*, June, 1975, p. 12.

The uses of vinyl chloride are discussed. PVC's carcinogenic effects on the human liver, lung and brain is cause for concern. The fact that cancer may not appear until many years after exposure to a carcinogen makes their detection and banning almost impossible. Major uses for PVC in the U.S. are listed.

Sharon, Nathan, "Glycoproteins," *Scientific American*, May, 1974, p. 78.

Proteins, with sugars linked to them as side chains, occur in blood plasma, enzymes, and hormones. Glycoproteins have been found in brain and nerve endings and may participate in memory. They act as antifreeze agents in the blood of Antarctic fish. The "sugar coating" on the surface of cells may determine their responses to viruses and to other chemicals. The chemical structure and formation of glycoproteins are discussed in detail.

Stroud, Robert M., "A Family of Protein Cutting Proteins," *Scientific American*, July, 1974, p. 74.

Enzymes that split proteins have various functions, from the digestion of food to blood clotting. Their common mode of action suggests that they had a common ancestor.

Watson, James D., *The Double Helix*, Atheneum Publishers, 1968.

In 1962, James Watson, Francis Crick, and Maurice Wilkins shared the Nobel Prize for their work in building a model of the DNA molecule. This book contains a fascinating personal account of the process by which the mystery was unravelled, including a description of the interpersonal relationships that developed among many members of the academic community.

PART SIX HORMONES, DRUGS, AND VITAMINS

OBJECTIVES

When you have finished Part Six, you will be expected to demonstrate acceptable performance on the following learning objectives:

1. Define the term *hormone*, and describe the functions of estrogens, androgens, and adrenal hormones in the human body.
2. Define the term *drug*.
3. Describe the physiological effects of depressants, stimulants, and hallucinogens on the human body.
4. Describe the similarities in chemical structures of various barbiturates, stimulants and hallucinogens, and their relationship to natural chemicals found in the human body.
5. Describe how an antimetabolite functions, with reference to sulfanilamide.
6. Describe how an antibiotic functions, with reference to penicillin.
7. Describe the functions of vitamins in human cell chemistry, and in general health.
8. Discuss the effects of insufficient amounts of Vitamins B, C, D, and niacin on humans.

INTRODUCTION

In this final section of the book, we will examine some biologically active organic compounds—those that act on the human body one way or another. These biologically active compounds include hormones, which the body synthesizes; vitamins, which the body requires but cannot synthesize, and which must be supplied by the diet; and drugs, some natural and some synthetic.

Some of the compounds mentioned in this part of the module may seem quite complex. However, remember that the chemical properties of any organic compound are determined in part by the overall structure of the compound, and in part by the compound's functional groups. You already know something about how shapes and functional groups affect the activity of organic compounds. Many of the synthetic compounds you will read about in this section have been developed by analyzing the structures and functional groups of known biologically active compounds, and producing new compounds which are similar.

The amount of material that can be included here is necessarily limited. After all, entire books have been written about hormones, drugs, and vitamins. This part of the module is intended to introduce you in a general way to just a few of these important compounds. Many of them may affect your life.

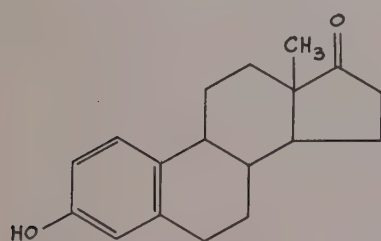
ORGANIC SECTION 6-1 HORMONES: THE BODY'S REGULATORS

Within various ductless glands of the body, called *endocrine glands* (ovaries, pituitary, adrenal glands, and the like), dozens of compounds are produced. These compounds, called *hormones*, are distributed from the glands to their "target" sites by the blood stream. Hormones are important because they control and regulate body processes. If any gland functions improperly and produces either too much or too little of a particular hormone, serious problems of hormone deficiency or hormone imbalance can result.

There are many, many different kinds of hormones, each characterized by a particular type of chemical structure. In this section, we'll examine the structures of two kinds of hormones—the sex hormones and the adrenal hormones.

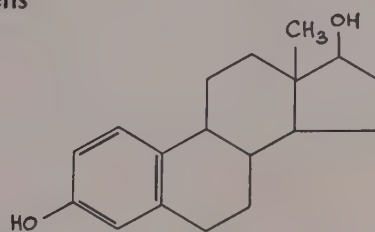
The Sex Hormones

The sex hormones not only control the development of the sex organs (ovaries and testes), but also the development and maintenance of the secondary sex characteristics—hair distribution, the menstrual cycle, breast development, and voice pitch. The sex hormones all share one important structural feature: they are *steroids*, compounds built around a particular four-ring carbon skeleton. The female sex hormones (estrogens) are produced in the ovaries; the male hormones (androgens) are produced in the testes. The structures of four sex hormones are shown below.

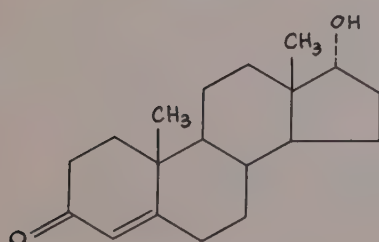


estrone

Estrogens

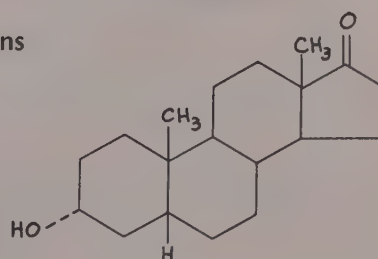


estradiol



testosterone

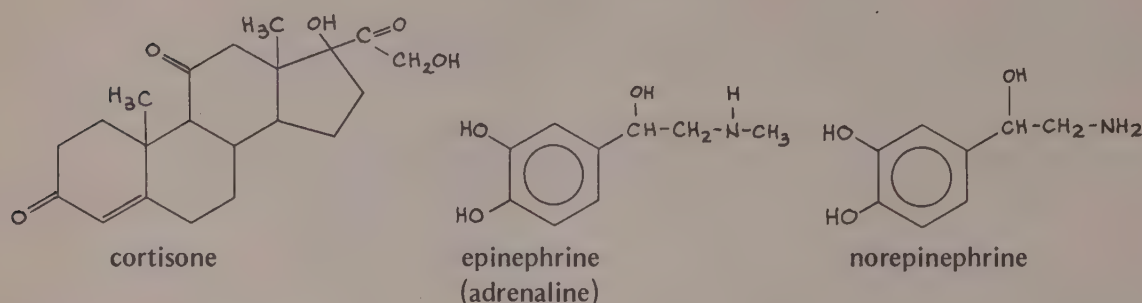
Androgens



androsterone

The Adrenal Hormones

The *adrenal glands*, located just above the kidneys, produce two types of hormones. The hormones produced in the outer portion of each gland (the adrenal cortex) are, like the sex hormones, steroids. The principal cortical hormone is cortisone. Hormones of the adrenal cortex affect carbohydrate metabolism and blood pressure. The hormones of the inner portion of each adrenal gland (the adrenal medulla) are epinephrine (adrenaline) and norepinephrine. These hormones affect muscle activity, blood pressure, and blood sugar level. Epinephrine production increases during anxiety, fear, or other stress. It prepares the body either to fight or to flee; thus it is sometimes called the fight/flight hormone.



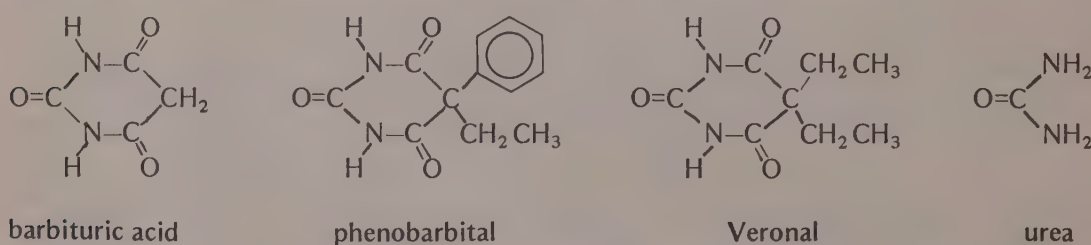
ORGANIC SECTION 6-2 DRUGS

Drugs are chemical substances which, when administered to an organism, affect its physical, mental, or emotional condition. Sometimes the effects are beneficial; sometimes they are not. Nearly all drugs are organic compounds, and frequently they have quite complex structures. Many drugs are natural compounds isolated from plant or animal material. Others are synthetic, designed by chemists to serve a particular function.

Depressant Drugs: Alcohol, Barbiturates, Sedatives

Drugs which slow down the nervous system and cause a decrease in mental and physical activity, often with a calming effect, are *depressants* (sometimes called sedatives). Some depressant drugs are called “downers.” The most widely used depressant is one that many people don’t think of as a drug at all—ethyl alcohol. This fact might surprise you, especially considering the exuberant behavior of some people when they are “under the influence”. Most people think of alcohol as a stimulant. However, the ultimate effect of having “one too many” is a deadening of the senses and drowsiness. Alcohol also causes blood vessels close to the skin to dilate. As a result, some people become flushed after drinking. People also tend to lose more body heat than usual after drinking. Can you explain why?

Barbituric acid and some of its derivatives, including phenobarbital and Veronal, are called *barbiturates*. The barbiturates are cyclic amides. Notice the relationship between their structures and that of urea (also an amide). Urea is the chief nitrogen-containing end product of protein metabolism, and one of the substances eliminated from the body in the urine.



Notice also that the six-membered ring common to the barbiturates is similar to that in the nitrogen bases thymine, cytosine, and uracil, components of the nucleic acids. (See pages 55–57).

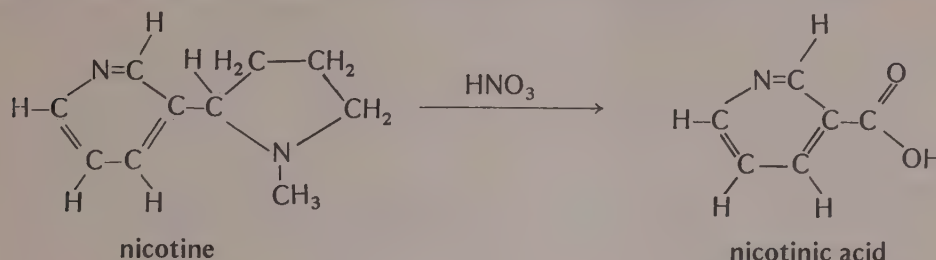
The effects of barbiturates resemble those of alcohol: You can get drunk on them; you can become addicted to them; you can suffer the same problems when you attempt to stop using them; and they can cause the same kind of hangover.

WARNING: A combination of barbiturates and alcohol can be 200 times more potent than either the barbiturate or the alcohol taken separately. Many people have died from this combined effect, called synergism. Although such deaths frequently are reported as an "overdose" of sleeping pills, they often are really a result of a combination of alcohol and barbiturates.

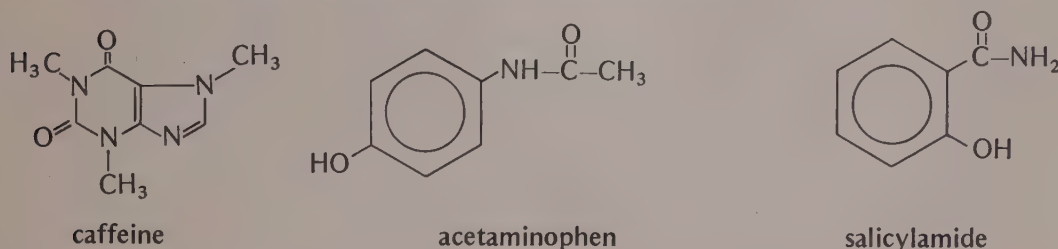
Stimulants

Compounds whose effects are the opposite of the depressants just described act as stimulants to the central nervous system. Stimulants are sometimes called "uppers". Some are used as appetite suppressants (diet drugs) and for warding off sleepiness.

One of the most widely used stimulants is *nicotine*, a component of tobacco. It is interesting to note that when nicotine is removed from cigarettes, most smokers no longer enjoy smoking them. In the laboratory, nicotine can be oxidized to nicotinic acid, a vitamin:

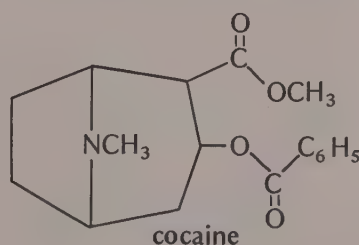


Another stimulant drug used daily by millions of people is *caffeine*. Caffeine is found in coffee, tea, and cola drinks. Sometimes it is combined with other drugs to enhance their effects. For example, *Anacin* contains aspirin and caffeine. *Excedrin*, which costs ten times as much as aspirin, contains acetaminophen, salicylamide, and caffeine.

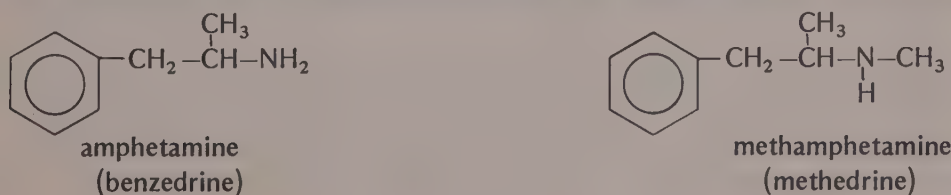


Some of these compounds are similar to aspirin in reducing fever and relieving pain. Whether there is any difference in the speed or effectiveness of a variety of pain relievers is controversial.

An old stimulant drug is *cocaine* ("coke"), an extract from the South American coca plant. Cocaine has been used for a long time. In fact, it is thought to have been used medicinally by the Incas as early as the 16th century. Today, the medicinal uses of cocaine have been supplanted by other drugs, but it is used in the underground drug culture.



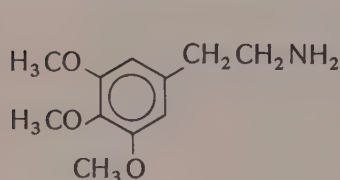
Even more commonly abused than cocaine are the synthetic drugs, the *amphetamines* ("speed"). The structural similarities of the amphetamines to epinephrine (page 60) should not go unnoticed.



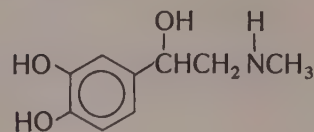
Hallucinogenic Drugs

Hallucinogens are compounds which produce changes in perception. However, these are usually not real hallucinations, since people under the influence of the drug can usually distinguish their visions from reality. These drugs are also referred to as "psychedelic".

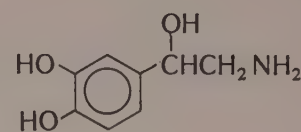
Perhaps the oldest hallucinogen is mescaline, which comes from the peyote cactus. Mescaline has been used by Indian tribes in the southwestern United States and Mexico for centuries. Its structure also closely resembles those of the amphetamines and the adrenal hormones, epinephrine (adrenaline) and norepinephrine. (See page 60.)



mescaline

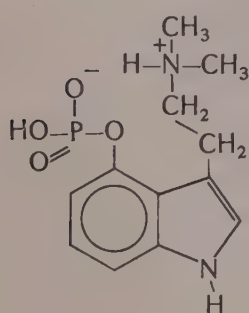


epinephrine

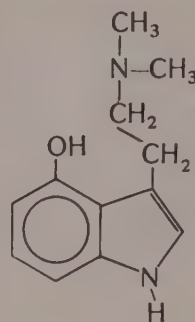


norepinephrine

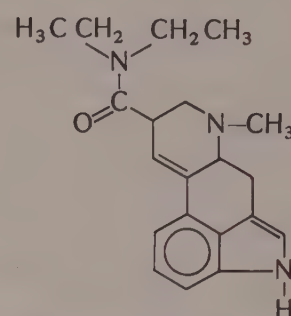
Other commonly used hallucinogens are psilocybin and psilocin, from certain Mexican mushrooms, and LSD (lysergic acid diethylamide), obtained by chemical transformations of a substance isolated from ergot, a fungus that grows on rye and wheat. Notice the structural similarities of these three compounds.



psilocybin



psilocin

lysergic acid diethylamide
(LSD)

Of perhaps greater significance, however, is the resemblance of these hallucinogens to serotonin, a substance found in various animal tissues, particularly the brain. These resemblances have given rise to the hypothesis that schizophrenia is caused by an imbalance in the metabolism of serotonin. Excitement and hallucinations might result from an excess of serotonin in certain regions of the brain, and depressive states from a deficiency of serotonin. Some evidence suggests that LSD blocks the ability of serotonin to transmit nerve impulses in the brain, and in some cases it can take over this function from serotonin.

The hallucinogens, "uppers" and "downers", become part of the illegal drug scene when people buy them without prescriptions. A person who becomes hooked on these drugs falls prey to buying drugs whose purity and dosages are unknown. All drugs can be dangerous (even fatal) if used incorrectly. Even nicotine, caffeine, and alcohol, drugs which are taken for granted by millions of people, have an effect on the body's chemistry. The effects of introducing foreign chemicals into the body vary widely among individuals. Some drugs may affect one person more than another.

Germ Killers: Chemotherapeutic Drugs

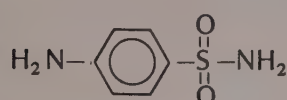
Chemotherapy is the use of chemicals to treat disease. In order to develop effective chemotherapeutic drugs, it is essential to find compounds which destroy the infecting organisms without harming the host.

When developing chemotherapeutic drugs, organic chemists usually start with some substance already known to possess chemotherapeutic activity. They prepare series of compounds of similar or related structure in the hope of finding compounds with enhanced activity. This approach assumes that chemotherapeutic activity is associated with particular structural features.

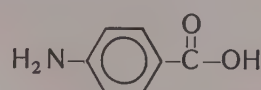
Also, it assumes that suitable changes in the structure of an active molecule may lead to more active compounds.

Antimetabolites are compounds which interfere with the metabolism within an organism. The structures of antimetabolites are closely related to a compound needed by the organism. They compete with, and take the place of, the needed compound. As a result, metabolism is blocked and the organism dies.

The best known antimetabolites are the sulfa drugs. Sulfanilamide, the earliest and best understood sulfa drug, was developed early in the 1930s. Its structure is very similar to that of *p*-aminobenzoic acid, a compound used by bacteria in the synthesis of folic acid.



sulfanilamide

*p*-aminobenzoic acid

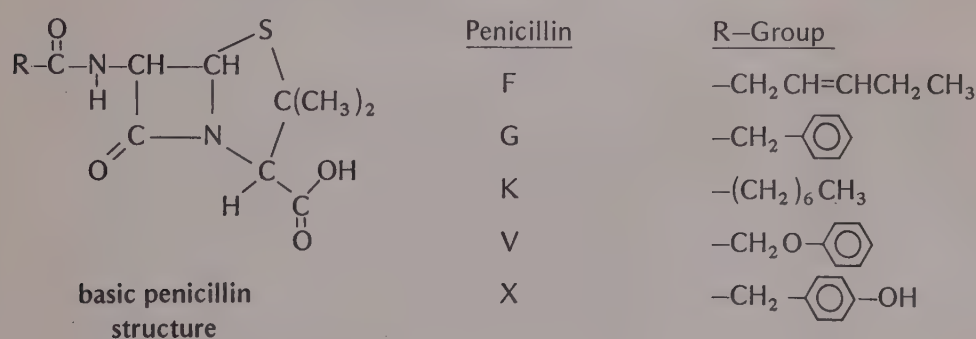
The bacteria accept the sulfanilamide, which interferes with their ability to synthesize folic acid, a required compound.

The sulfa drugs are relatively harmless to us because we do not synthesize folic acid. Instead, we obtain folic acid in our diets. However, in some individuals, some side effects, including anemia, do result from the use of sulfa drugs. In fact, some people have allergic reactions to sulfa drugs. Therefore, these drugs cannot be administered indiscriminately.

An *antibiotic* is a compound synthesized by one microorganism which is toxic to another microorganism. Many of these can now be synthesized in the laboratory. Many of the original antibiotics have been altered in the laboratory to make them more effective or more useful in special circumstances.

The first successful antibiotics were the penicillins, compounds produced by the mold *Penicillium*. They were discovered by accident in 1928 by Alexander Fleming, an English bacteriologist. By 1938 Ernst Chain and Howard Flory had isolated a pure form of penicillin and used it as an antibiotic. The three scientists shared a Nobel Prize in 1945.

There are several natural penicillins whose structures differ only in the R-group:



Notice the highly strained ring system—a four-membered ring attached to a five-membered ring. If you examine these rings closely, you will see that they are composed of two amino acids, valine and cysteine.

Over a long period of time, some strains of bacteria have evolved that are penicillin-resistant. As a result, a number of new penicillins have been synthesized that are effective against these resistant bacteria.

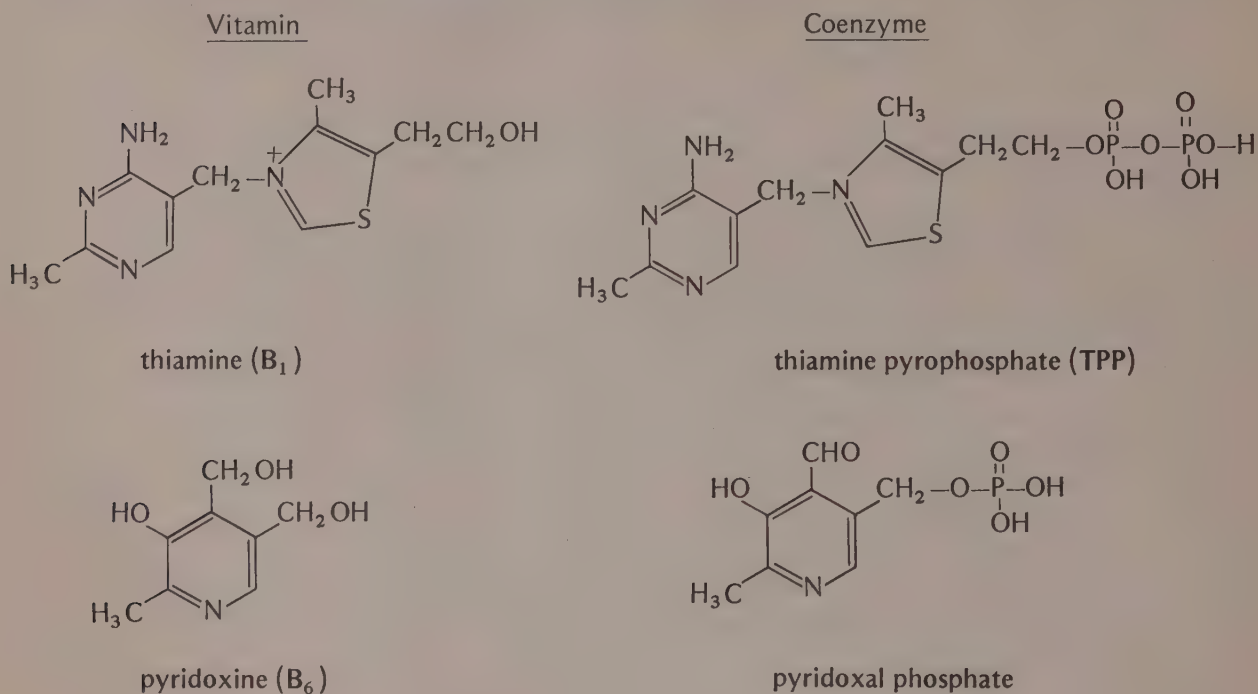
The penicillins, like the sulfa drugs, are not totally harmless. Many people, in fact, have rather severe allergic reactions to penicillins. However, they are still one of the most effective and widely used groups of antibiotics.

Today, the medical profession makes use of a wide variety of antibiotic drugs other than the penicillins. Some of the antibiotics you may have heard of are Streptomycin, Terramycin, Aureomycin, and Erythromycin. However, the search for new antibiotics continues. Why do you suppose it is necessary to continue developing new antibiotics?

ORGANIC SECTION 6-3 VITAMINS

To understand the role of vitamins in human nutrition, we must first understand the role of *enzymes*, which are organic catalysts. A catalyst is a substance which lowers the activation energy, E_{act} , for a chemical reaction. (See Section 1-3.) When the activation energy is lowered the reaction goes faster. Enzymes are catalysts for biological reactions. Reactions which would normally proceed slowly in the absence of enzymes go one hundred to one million times faster in their presence. Enzymes are absolutely essential for making the reactions in our bodies occur.

Enzymes are primarily proteins. Many enzymes, however, do not function in the absence of a partner, a *coenzyme*. This is where vitamins enter the picture. Many vitamins, a few of which are shown below, serve as structural units for specific coenzymes.

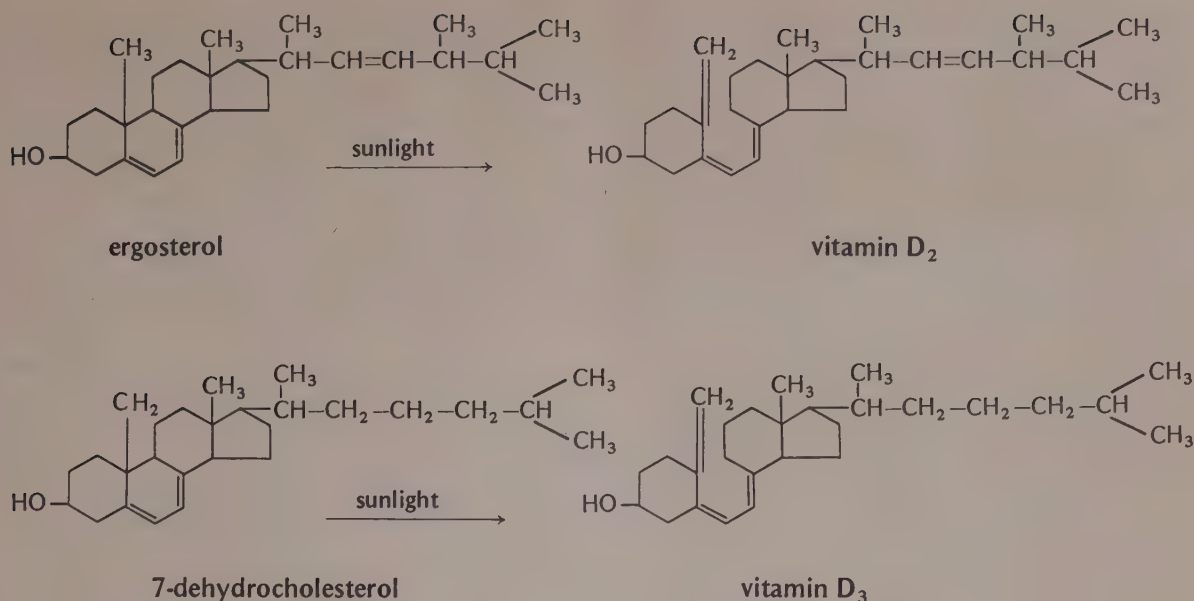


Vitamins cannot be synthesized in our bodies. Therefore, we must obtain them from our food. A well-balanced diet generally supplies all the vitamins we need. For those of us who don't eat what we should, vitamin capsules are available to supplement our inadequate diets.

Notice how many foods these days come labelled "vitamin enriched." This usually means that the vitamins that occur naturally in the food have been destroyed by processing, and the food processor has put some or all of them back in at a later stage. Bread and cereals are the most common examples. When whole wheat is converted into white flour, almost all the vitamins are destroyed. Therefore, white bread is usually "enriched" to replace some of the lost vitamins.

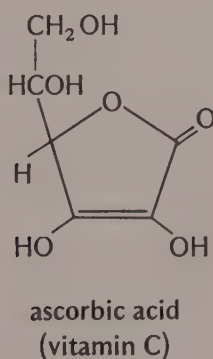
The essential nature of vitamins can be illustrated by some examples from medical history. During the late 1800s people on the island of Java suffered from a disease called *beriberi*. This disease causes degeneration of the nerves, the digestive system, and the heart. Efforts to find the organism responsible for the disease failed. The cause was finally traced to the refined rice that most of the people ate. When the Javanese returned to eating brown rice, the disease disappeared. Now we know that refining (polishing) rice removes the outer bran coating, including most of the rice's vitamins. The essential vitamin in unpolished rice is thiamine, vitamin B_1 , shown above.

Rickets, a childhood disease characterized by softening of the bones and often associated with malnutrition, can be caused by a deficiency in either vitamin D or calcium. Rickets, like beriberi, can be reversed by the intake of a vitamin. In this case, the essential vitamin is vitamin D, which today is added to most milk. In addition, if the steroid alcohols ergosterol and 7-dehydrocholesterol are supplied by the diet, the body can convert them to vitamins D_2 and D_3 . The conversion takes place when the skin is exposed to sunlight:



Notice how these two related vitamins differ only by a double bond and by a methyl group in the side chain of the five-membered ring.

Scurvy, a disease characterized by spongy gums, loose teeth and bleeding skin was first recorded by English sailors in the 1500s. In 1593 it was discovered that the disease could be cured by drinking orange or lemon juice. The cure was unfortunately forgotten, but some 200 years later, limes were accidentally ordered in the rations for English sailors (subsequently nicknamed "limeys"). It was observed that these sailors did not get scurvy. The essential vitamin that prevents scurvy is now known to be ascorbic acid, vitamin C.



Most of us have grown up knowing we should drink citrus fruit juice regularly. There is current speculation and evidence that larger amounts of vitamin C can prevent colds, or at least cause the cold symptoms to be milder and the cold to disappear faster. Linus Pauling, a Nobel-Prize-winning chemist, is the best known proponent for this use of vitamin C.

Nicotinic acid (page 61), also known as niacin, is a vitamin which prevents a disease called *pellagra*. Niacin is found in foods such as liver, peanuts, and wheat germ. There is no evidence that naturally occurring nicotinic acid comes from nicotine.

The function of vitamins is still not fully understood. In many cases, even the amount of particular vitamins necessary for the body to function normally (the Minimum Daily Requirement—MDR) is unknown. An overdose, in some cases, can be as dangerous as a deficiency. Excess vitamin D can cause calcium to deposit in tissues other than bone—the heart, for example. Excess vitamin A intake can cause headaches, skin problems, weakness, and painful areas along various bones. Fortunately, safe doses of vitamins occur naturally in foods, and a healthy body can dispose of most excesses with little difficulty.

SUMMARY, PART SIX

Living organisms are chemical systems. Life continues for any individual organism as long as its chemical processes are continuing normally. In this part of the module you have read about a number of chemicals which have an effect on one or another of the normal life processes. Some of these biologically active chemicals are essential parts of the normal process. Their absence or deficiency leads to illness. Other biologically active chemicals slow or increase the rate of basic processes. Still others interfere with one or more of the processes.

From a chemist's point of view, a substance should be used only if it enhances the effective function of the human organism. This view rules out the indiscriminate use of substances of questionable purity under uncontrolled situations.

SUGGESTIONS FOR FURTHER STUDY

1. Vitamin C is a substance that you can prepare in the laboratory. Consult your teacher about where to obtain a set of directions for its preparation.
2. Urea is a waste product of human metabolism. Find out what you can about the chain of reactions that produces it.
3. Examine the structures of the drugs described in this chapter, and compare their structures with those of various amino acids and other substances found in the human organism.
4. One subject not considered in this module is the chemistry of poisons. In some cases, even a minute amount of a substance may prove lethal. Other substances may be beneficial in small amounts, but poisonous if taken in large doses. Some highly poisonous substances are prescribed as medicines. Investigate the chemistry of some poisonous and potentially poisonous substances, and find out what determines their toxicity.

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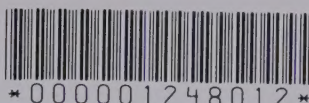
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